FOOD BIOCHEMISTRY

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References

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What is food biochemistry?

- Concerns about food exist everywhere
  -in developing countries: most people are involved in food production
  YET: adequate amounts remain an ever-present problem
  -in developed countries: few people are involved in food production; highly mechanised
  YET: food is available in abundance and is processed; chemical additives are commonly used; major concerns: price, quality, variety, effects of processing and added chemicals on nutritive value and safety
- Food science deals with the physical, chemical and biological properties of food in relation to stability, cost, quality, processing, safety, nutritive value
  ⇨ food science is an interdisciplinary subject involving bacteriology, chemistry, biology, engineering, economy, safety, *etc*.
- Food biochemistry deals with composition and properties of food and the chemical changes during processing, storage and handling
  ⇨ food biochemistry is thus related to chemistry, physiology biology, molecular biology, *etc*.
- Major concerns: food quality and food safety

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TABLE 1 Classification of Alterations That Can Occur in Food During Handling, Processing, or Storage

Attribute	Alteration
Texture	Loss of solubility Loss of water-holding capacity Toughening Softening
Flavor	Development of: Rancidity (hydrolytic or oxidative) Cooked or caramel flavors Other off-flavors Desirable flavors
Color	Darkening Bleaching Development of other off-colors Development of desirable colors (e.g., browning of baked goods)
Nutritive value	Loss, degradation or altered bioavailability of proteins, lipids, vitamins, minerals
Safety	Generation of toxic substances Development of substances that are protective to health Inactivation of toxic substances

From: "Food Chemistry" (1996) OR Fennema, ed.

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TABLE 2 Some Chemical and Biochemical Reactions That Can Lead to Alteration of Food Quality or Safety

Types of reaction	Examples
Nonenzymic browning	Baked goods
Enzymic browning	Cut fruits
Oxidation	Lipids (off-flavors), vitamin degradation, pigment decoloration, proteins (loss of nutritive value)
Hydrolysis	Lipids, proteins, vitamins, carbohydrates, pigments
Metal interactions	Complexation (anthocyanins), loss of Mg from chlorophyll, catalysis of oxidation
Lipid isomerization	Cis → trans, nonconjugated → conjugated
Lipid cyclization	Monocyclic fatty acids
Lipid polymerization	Foaming during deep fat frying
Protein denaturation	Egg white coagulation, enzyme inactivation
Protein cross-linking	Loss of nutritive value during alkali processing
Polysaccharide synthesis	In plants postharvest
Glycolytic changes	Animal tissue postmortem, plant tissue postharvest

From: "Food Chemistry" (1996) OR Fennema, ed.

TABLE 3 Cause-and-Effect Relationships Pertaining to Food Alterations During Handling, Storage, and Processing

Primary causative event	Secondary event	Attribute influenced (see Table 1)
Hydrolysis of lipids	Free fatty acids react with protein	Texture, flavor, nutritive value
Hydrolysis of polysaccharides	Sugars react with proteins	Texture, flavor, color, nutritive value
Oxidation of lipids	Oxidation products react with many other constituents	Texture, flavor, color, nutritive value; toxic substances can be generated
Bruising of fruit	Cells break, enzymes are released, oxygen accessible	Texture, flavor, color, nutritive value
Heating of green vegetables	Cell walls and membranes lose integrity, acids are released, enzymes become inactive	Texture, flavor, color, nutritive value
Heating of muscle tissue	Proteins denature and aggregate, enzymes become inactive	Texture, flavor, color, nutritive value
Cis → trans conversions in lipids	Enhanced rate of polymerization during deep fat frying	Excessive foaming during deep fat frying; diminished bioavailability of lipids

From: "Food Chemistry" (1996) OR Fennema, ed.

Carbohydrates

CARBOHYDRATE

= SACCHARIDE (< Greek *sakcharon*)

= SUGAR

= $C_nH_{2n}O_n$

- *Monosaccharides*
  Named: xx-<u>*ose*</u>
- *Oligosaccharides* (di-, tri-, …saccharides)
- *Polysaccharides*

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Monosaccharides

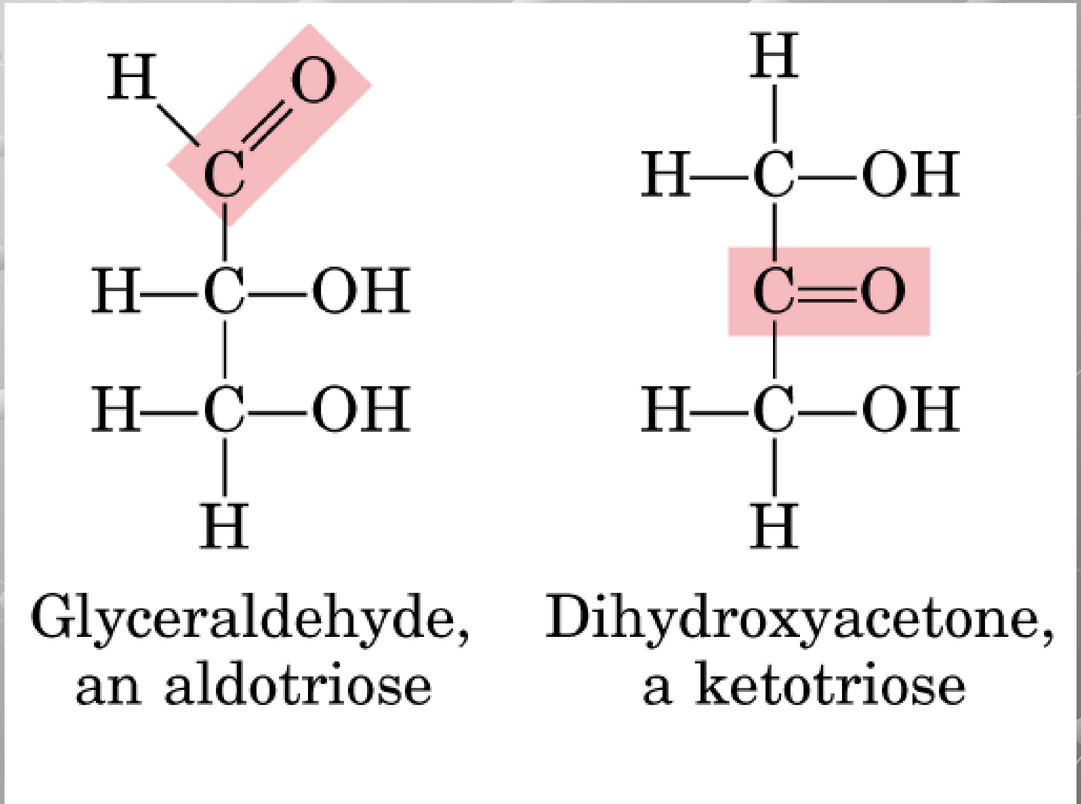
Two families:

- **ALDOSES**

(carbonyl group at the end of the chain: *aldehyde*)

- **KETOSES**

(carbonyl group at any other position: *ketone*)



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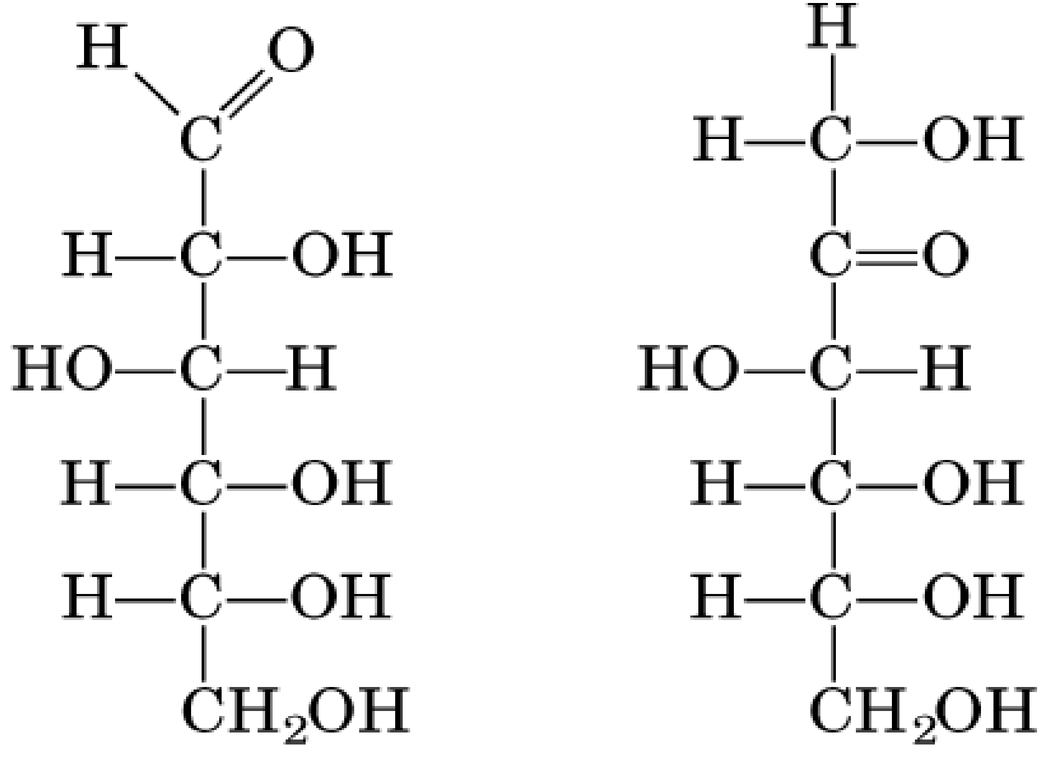
Other example: two common hexoses



D-Glucose,
an aldohexose

D-Fructose,
a ketohexose

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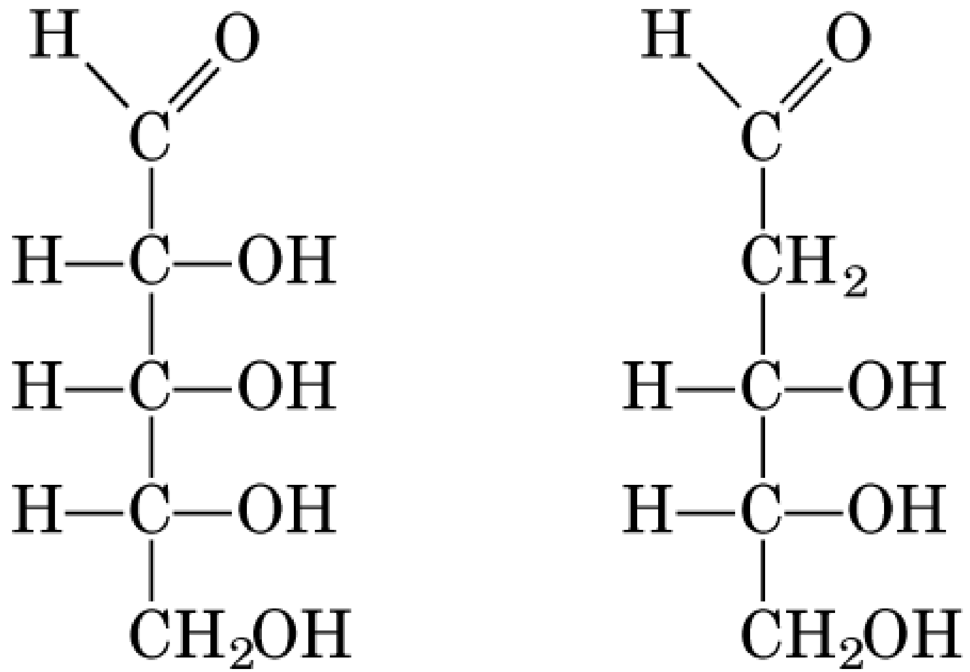
Pentose components of nucleic acids: D-ribose is a component of ribonucleic acids (RNA), and 2-deoxy-D-ribose is a component of deoxyribonucleic acids (DNA)



D-Ribose, an aldopentose

2-Deoxy-D-ribose, an aldopentose

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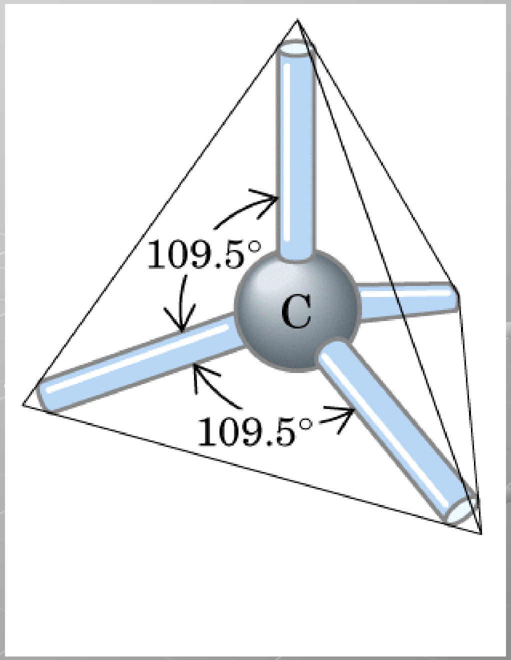
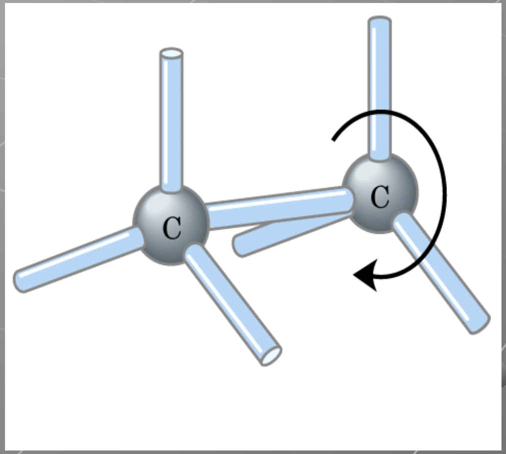
Carbon

Some facts:

Carbon atoms have a characteristic tetrahedral arrangement of their four single bonds



Carbon-carbon single bonds have freedom of rotation



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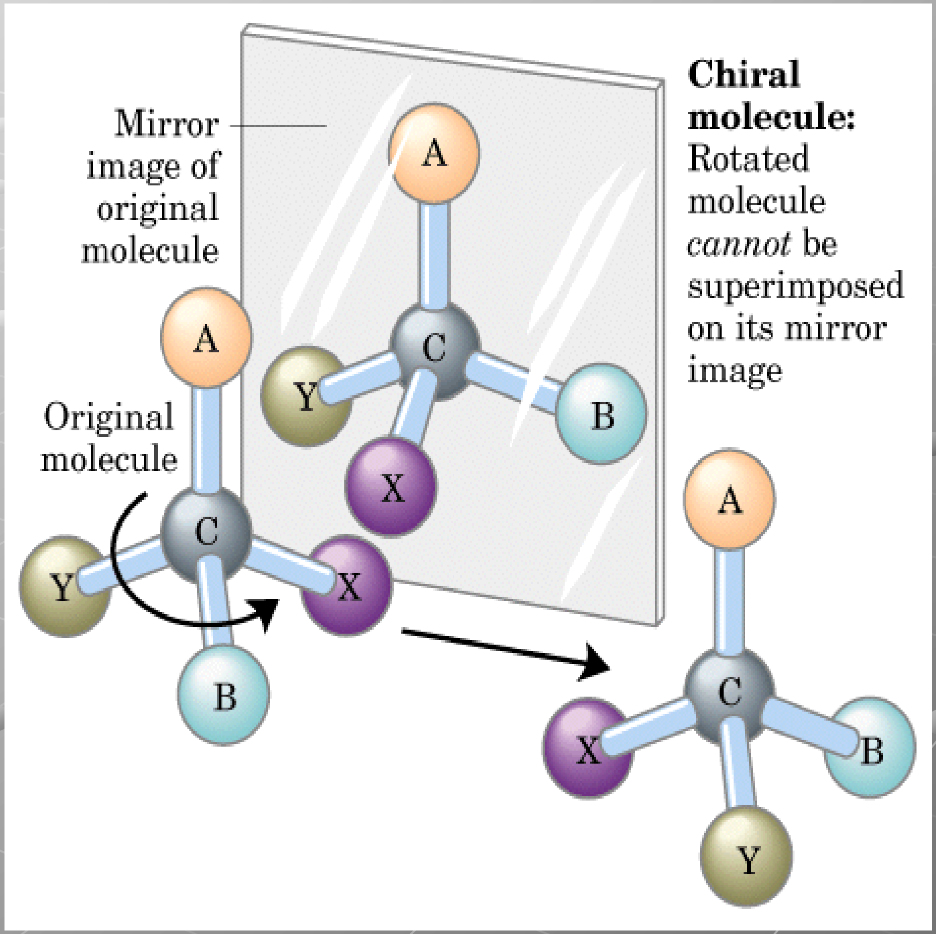
When a carbon atom has four different substituent groups (A, B, X & Y), they can be arranged in two ways that represent **non-superimposable** mirror images of each other (called "**enantiomers**")



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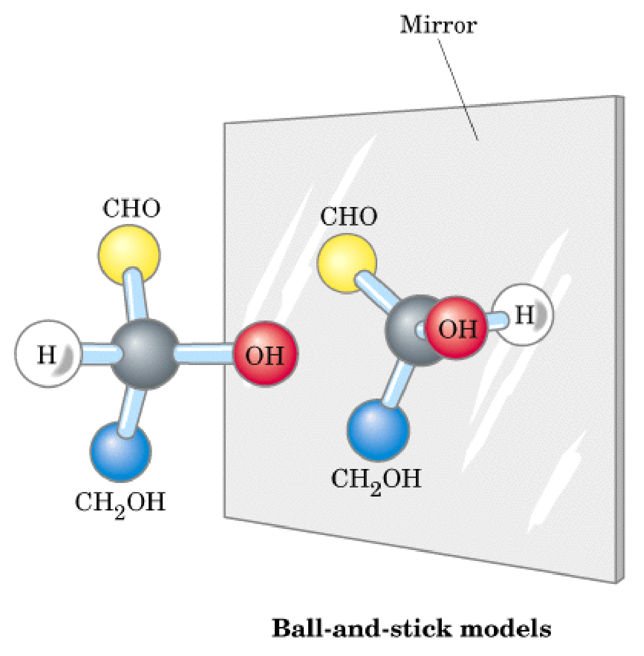
Monosaccharides have asymmetric centers

Monosaccharides have several asymmetric ("***CHIRAL***") carbon atoms

they occur in optically active isomeric forms

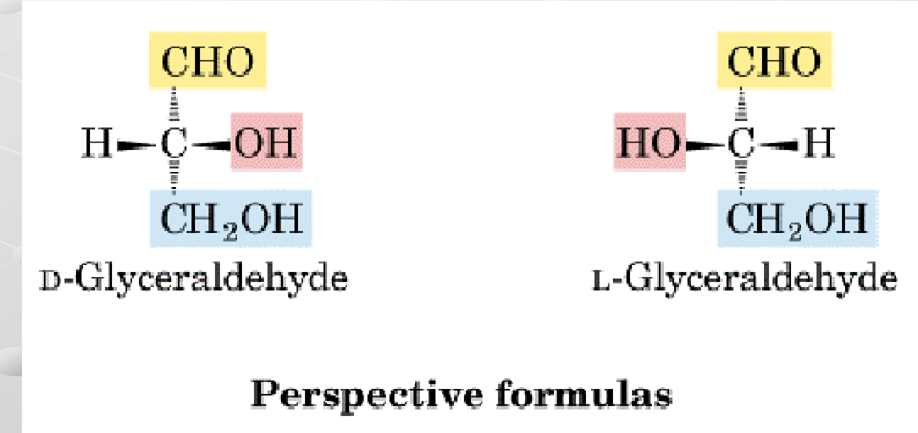
The simplest aldose is <u>glyceraldehyde</u>
It contains <u>one</u> chiral center, and occurs in <u>two</u> optical isomers or *enantiomers*:

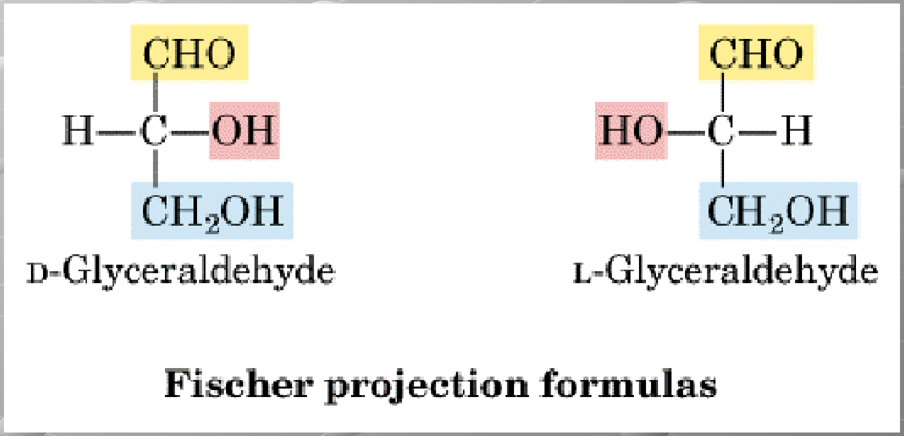


<u>BY CONVENTION:</u>
one of them is called the D-isomer, the other the L-isomer
<u>D</u>-isomer: —OH to the right (<*Latin, <u>D</u>exter*)
<u>L</u>-isomer: —OH to the left (<*Latin, <u>L</u>aevus*)

To represent three-dimensional sugar structures on paper, we often use:

Fisher projection formulas





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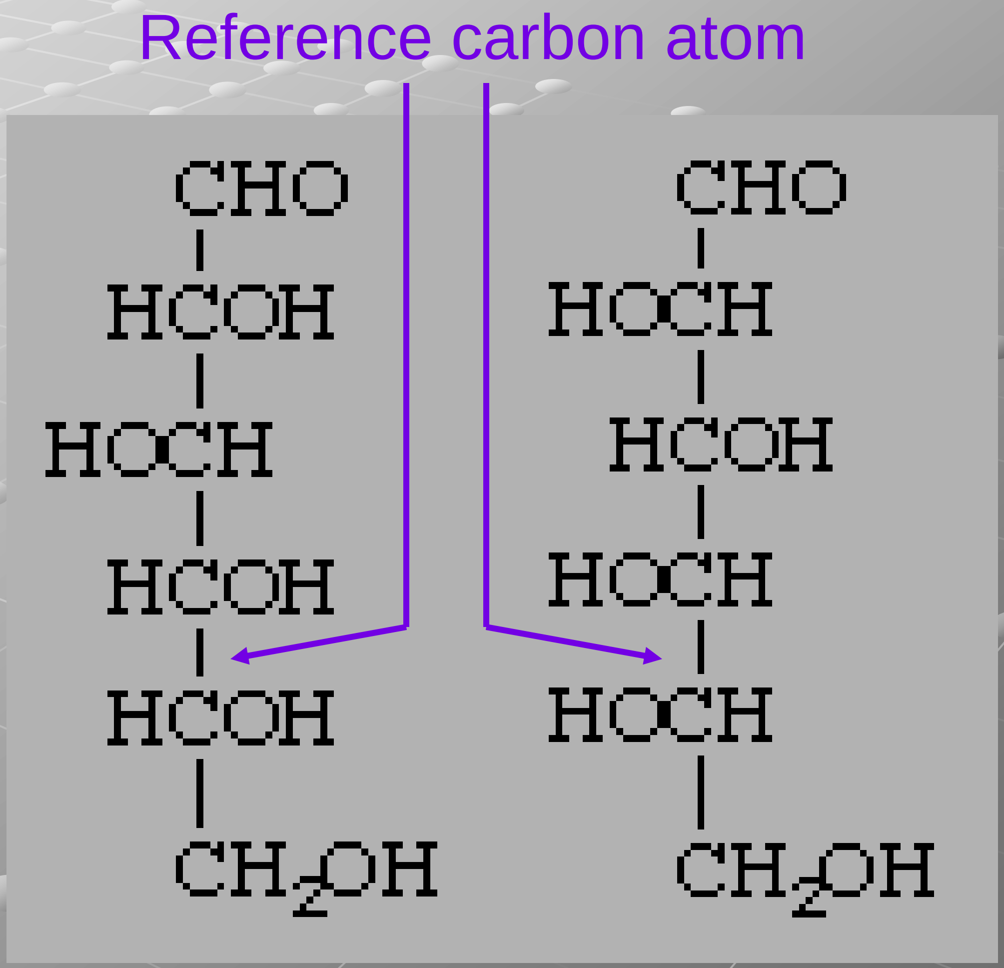
BY CONVENTION:

horizontal bonds project *out of the plane* of the paper,
vertical bonds project *behind the plane* of the paper.

Molecules with <u>n</u> chiral centers can have <u>2^n</u> stereoisomers

The stereoisomers of monosaccharides can be devided into two groups that differ in the configuration at the chiral center that is *most distant* from the carbonyl carbon.

The latter chiral center is called <u>*the reference carbon atom*</u>.



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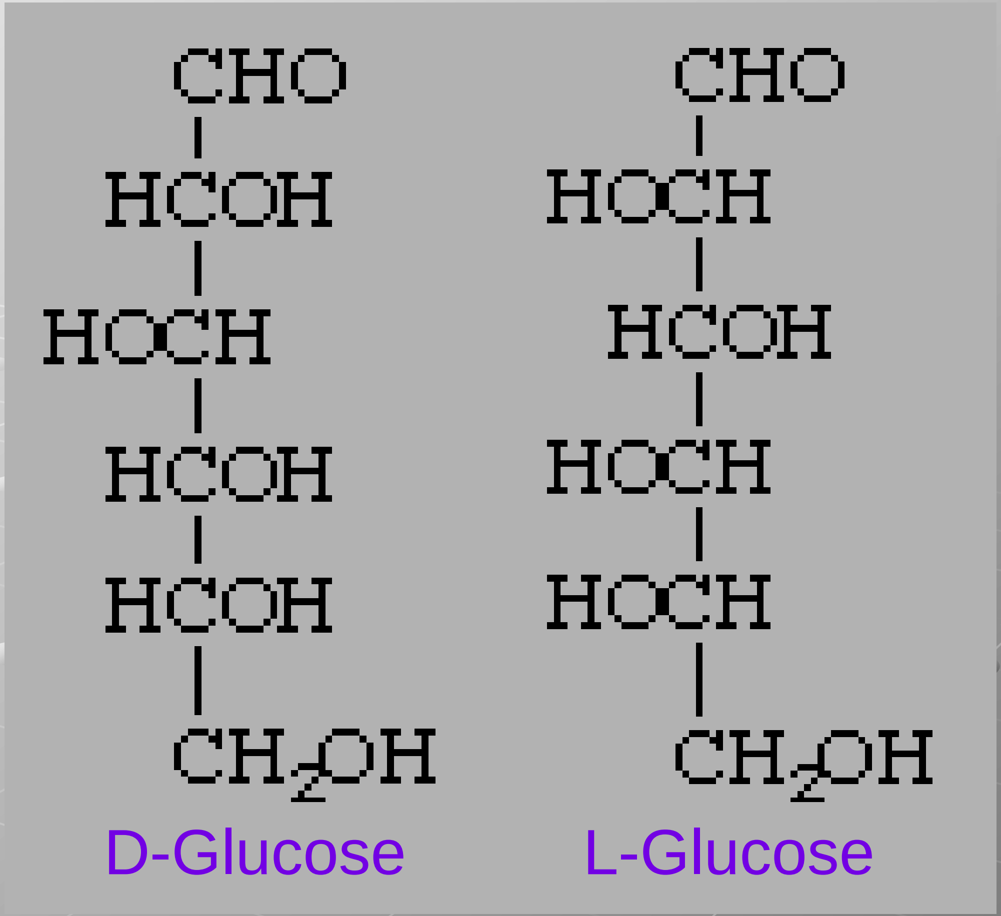

BY CONVENTION:

The sugar is called a ***D-sugar*** when the –OH at the reference carbon is ***on the right*** in the Fischer projection formula

The sugar is called an ***L-sugar*** when the –OH at the reference carbon is ***on the left*** in the Fischer projection formula

Most hexoses of living organisms are D-isomers.

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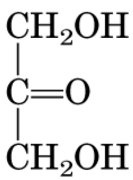
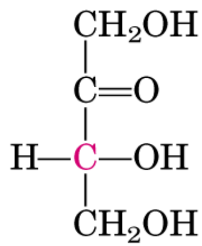
Series of D-Ketoses:

Three carbons



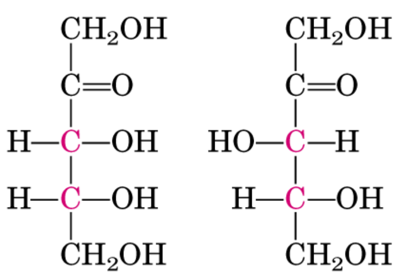
Dihydroxyacetone

Four carbons



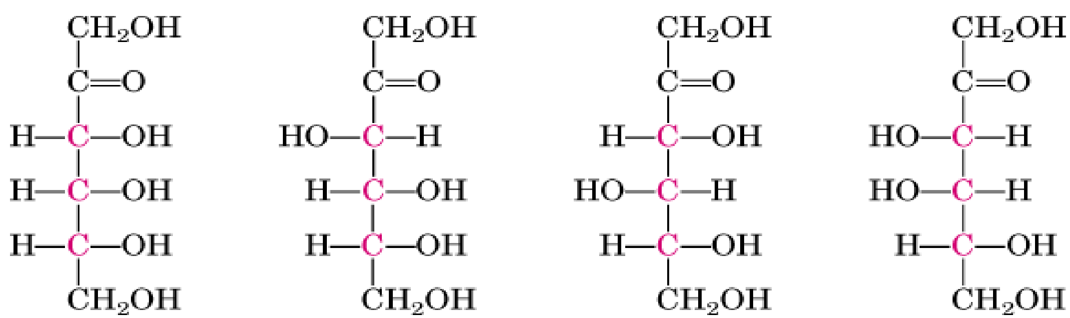
D-Erythrulose

Five carbons



D-Ribulose D-Xylulose

Six carbons



D-Psicose D-Fructose D-Sorbose D-Tagatose

Carbon atoms in red are chiral centers
Sugars in boxes are most common in nature

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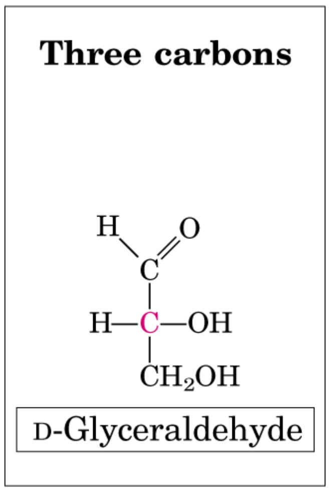
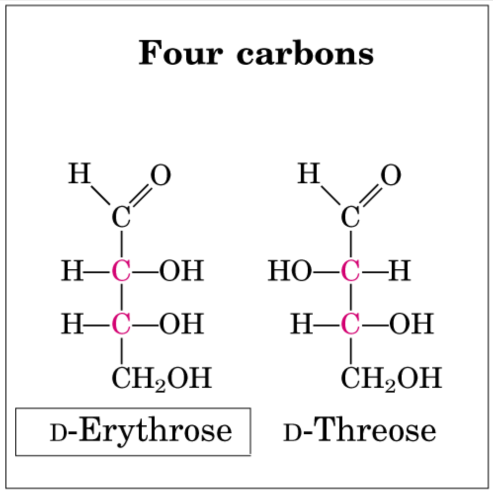
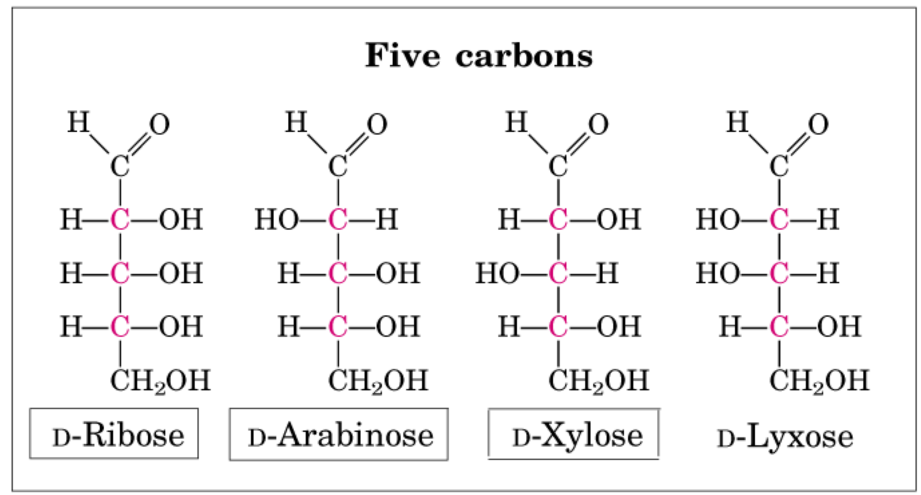
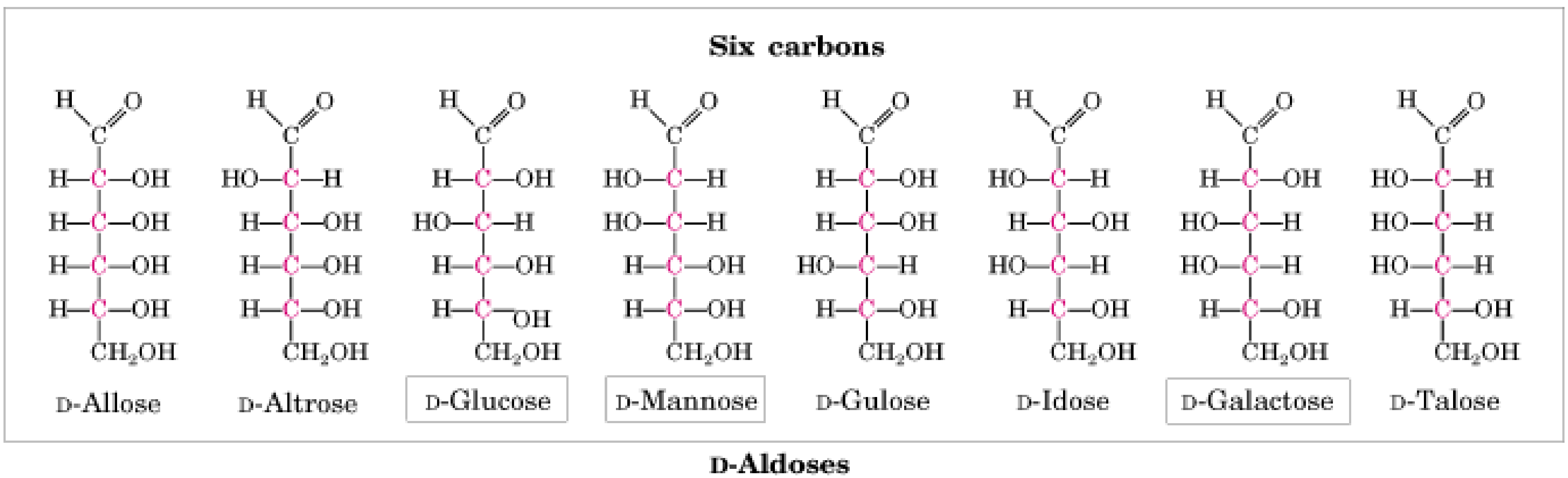
Series of D-Aldoses:









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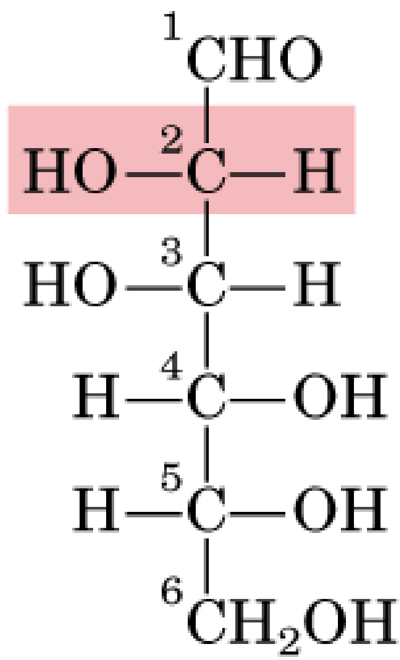
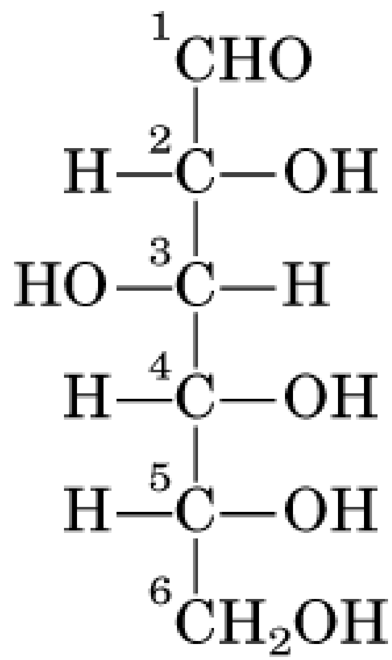
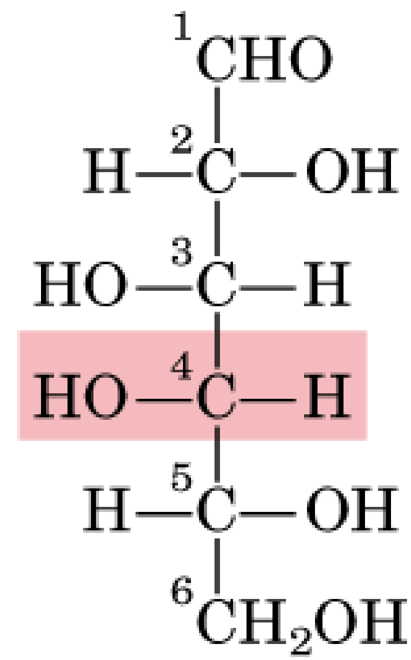
Two sugars that differ only in the configuration around one single carbon atom are called: epimers



D-Mannose
(epimer at C-2)



D-Glucose



D-Galactose
(epimer at C-4)

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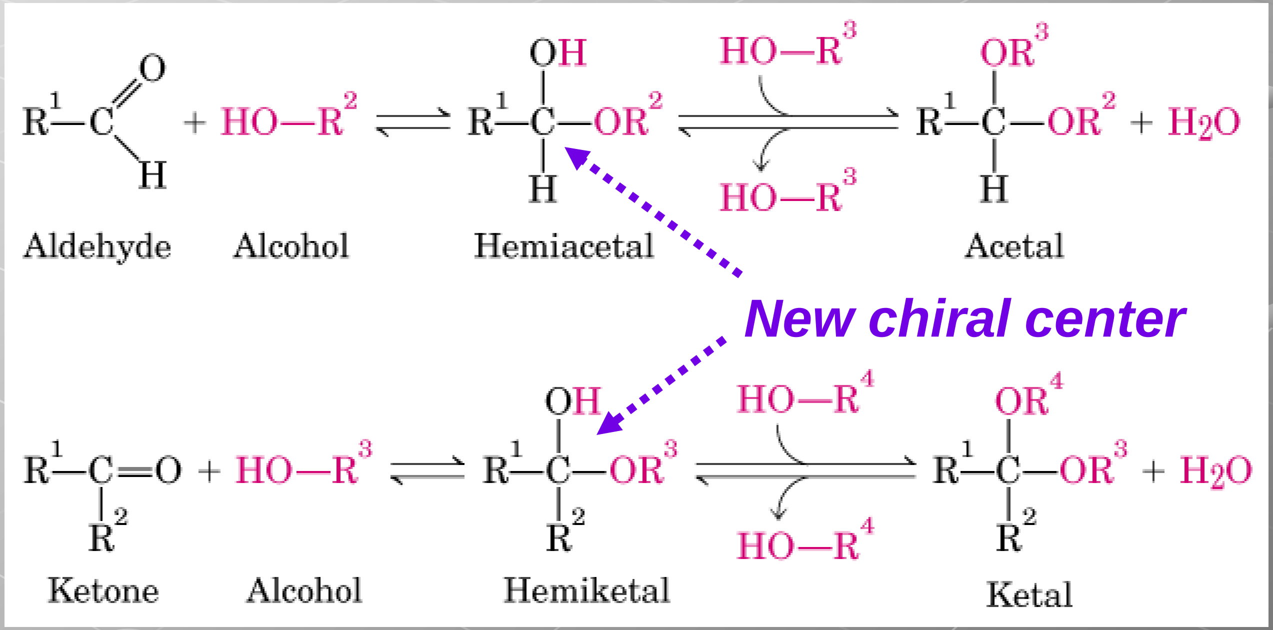
The common monosaccharides have cyclic structures

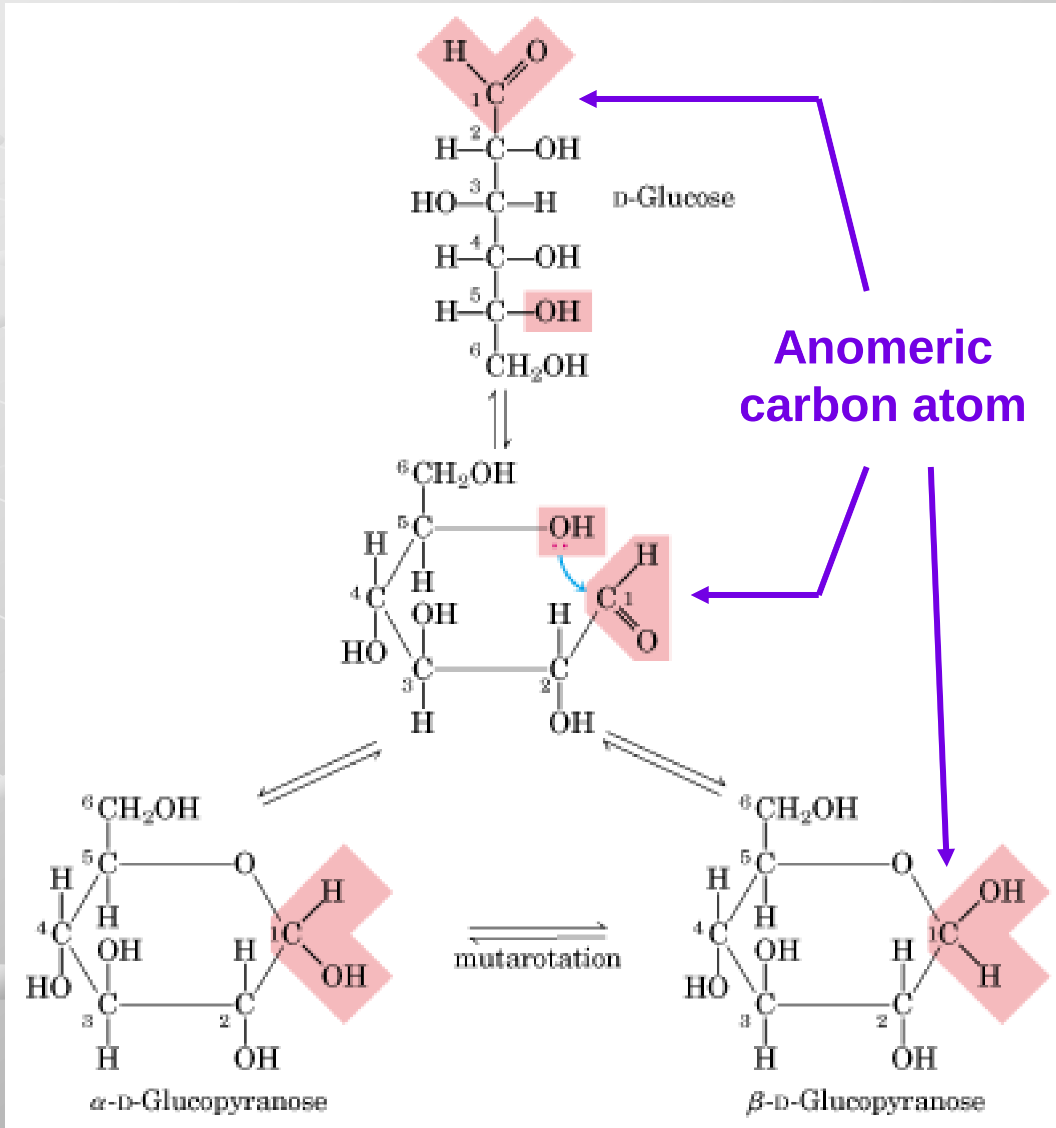
In aqueous solutions, sugars with four, five or more C-atoms in the backbone predominantly occur as cyclic (ring) structures.

The formation of these ring structures is based on a general reaction between aldehydes (ketones) and alcohols, to form resp. ***hemiacetals*** (***hemiketals***):



These hemiacetals/hemiketals contain a ***new asymmetric carbon atom***, thus they can exist in two stereoisomeric forms

Example:
Formation of the two cyclic forms of D-glucose



In solution, the ring structure is in equilbrium with the open (straight-chain) form.

The carbonyl carbon atom is called the **anomeric** carbon atom.

The stereoisomers are designated the α-(*alpha*) and β-(*beta*) anomers. The interconversion of α- and β-anomers is called **mutarotation**.

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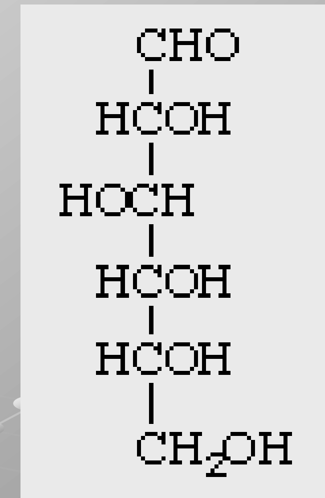
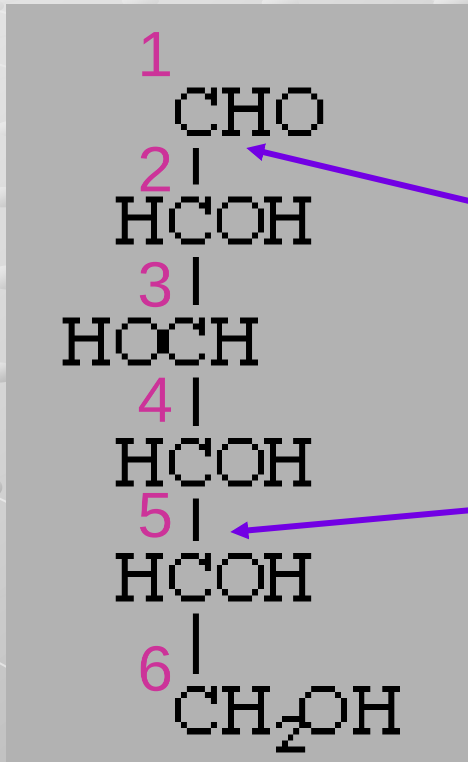
Rules for ring formation

Example:
D-glucose



1. Number the C-atoms in <u>Fischer</u> projection:



anomeric carbon atom (C1)

C2-5 are asymmetric

reference carbon atom (C5)
i.e. the last asymmetric C-atom before the CH_2OH

2. Check the position of the –OH at the reference C-atom.
(You will need this information later)

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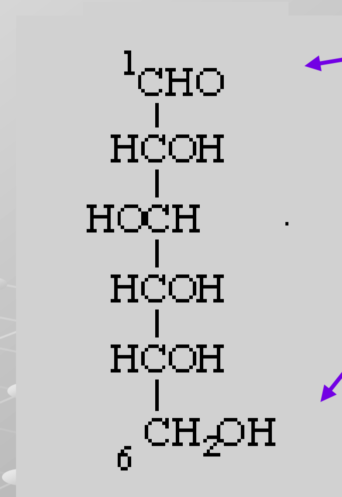
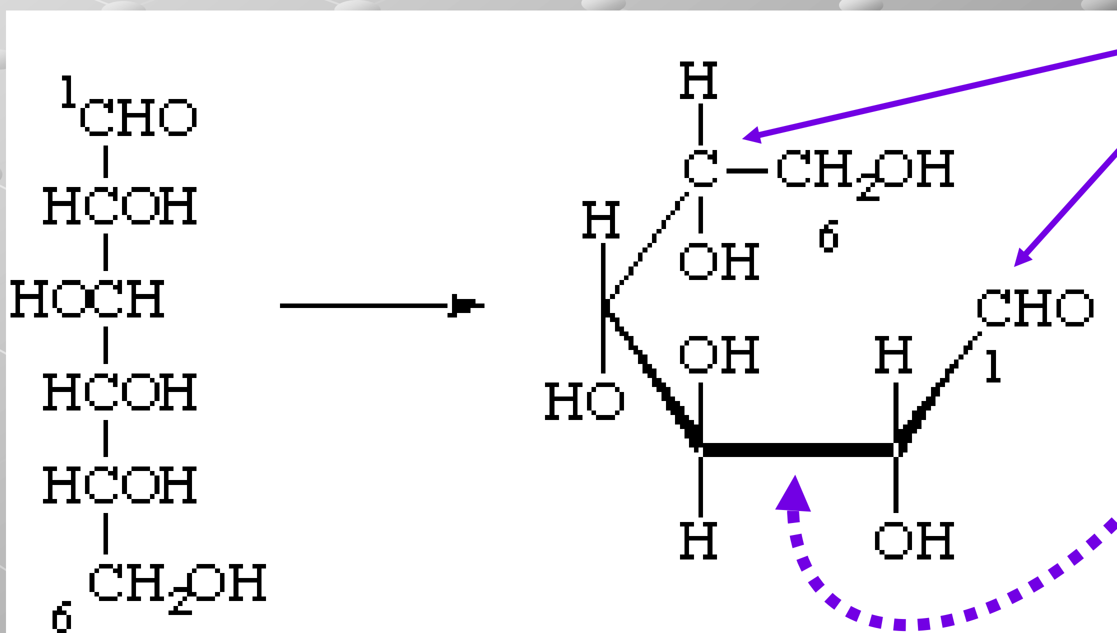
3. **<u>Convert the Fischer projection into the Haworth projection</u>** by starting to write down the molecule in the following way:



head

tail

i.e.:



reference carbon

anomeric carbon

heavy line, meaning that this bond is nearest to the observer

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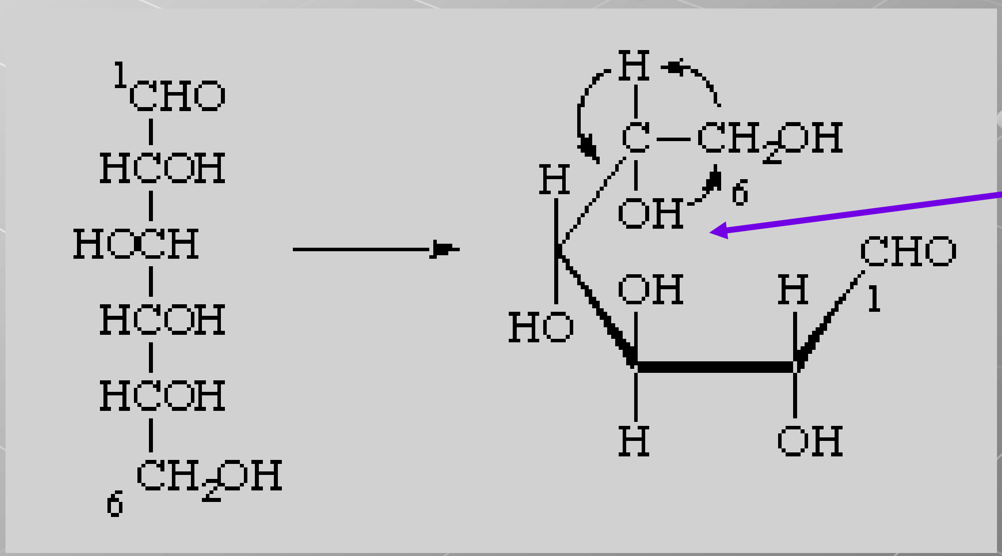
4. Place the –OH groups at the correct positions (*i.e. above or below the plane of the emerging sugar ring*), taking into account that:

Fisher projection	→	Haworth projection
RIGHT		UNDER
LEFT		ABOVE

5. Start counting from the anomeric carbon atom to trace the –OH to be used for ring closure.
This will be determined by the kind of ring (5-, or 6-ring) that will be formed.

6. Circularly permute the groups on the last carbon atom, in such a way that the future ring oxygen is facing to the right:



future ring oxygen, if a 6-ring is to be formed

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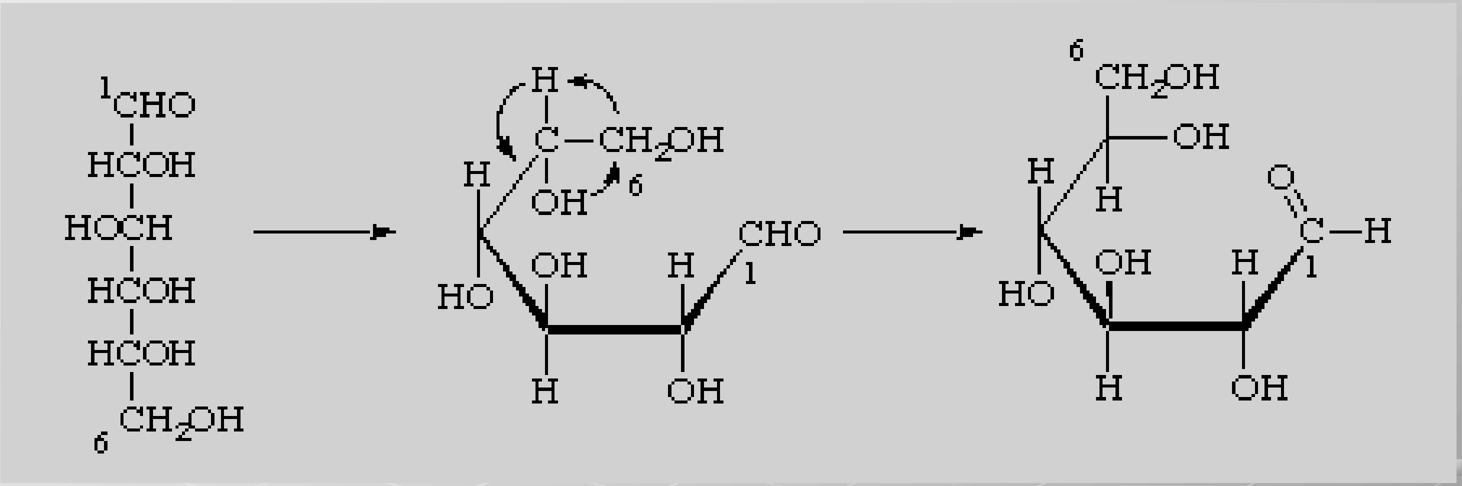
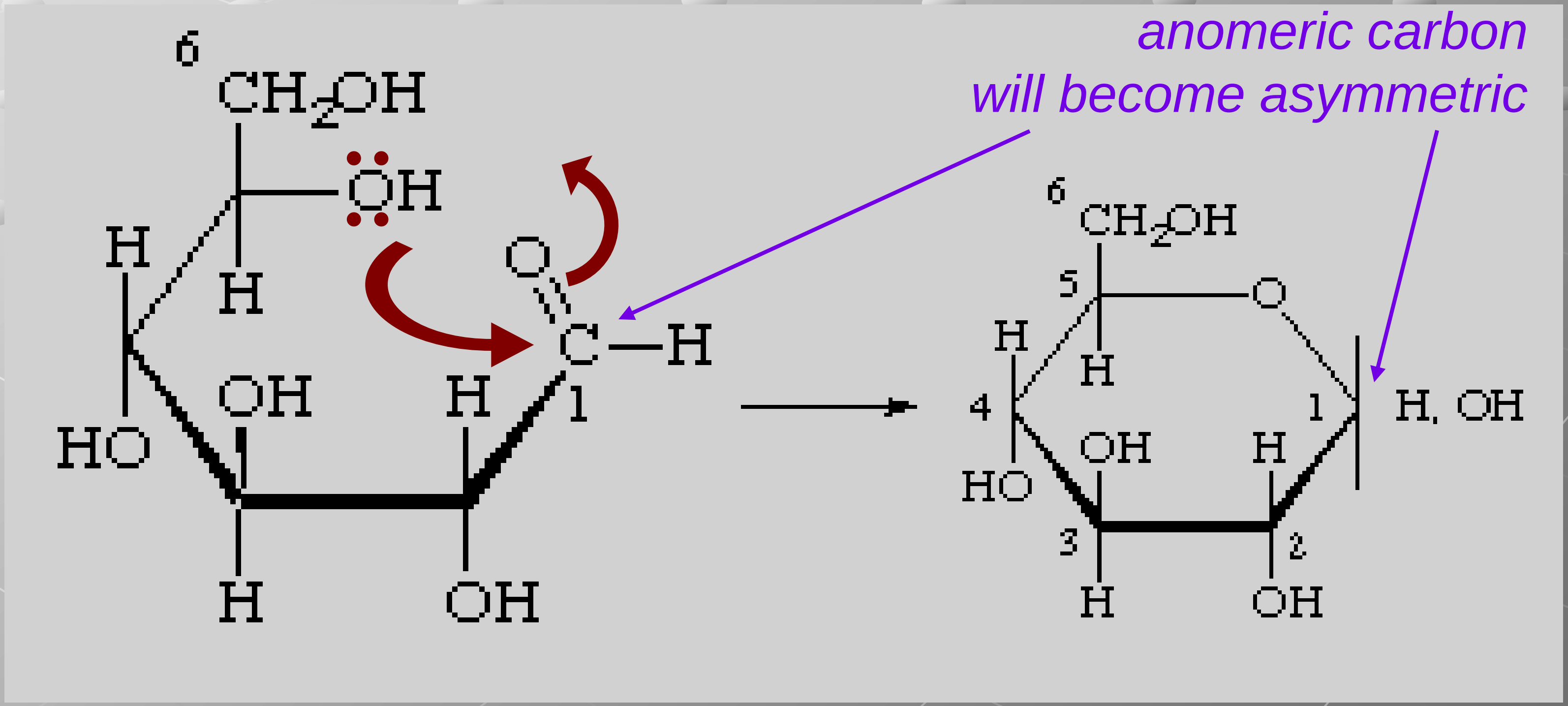


7. Close the ring, and rewrite the structure:



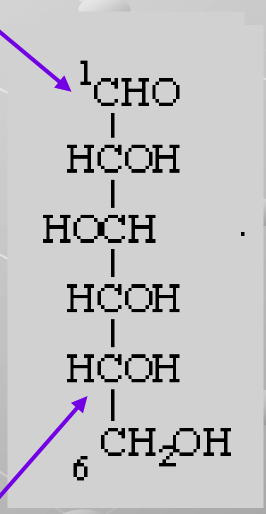
8. Finally determine whether the –OH group at the anomeric carbon atom is above, or below the plane of the ring:

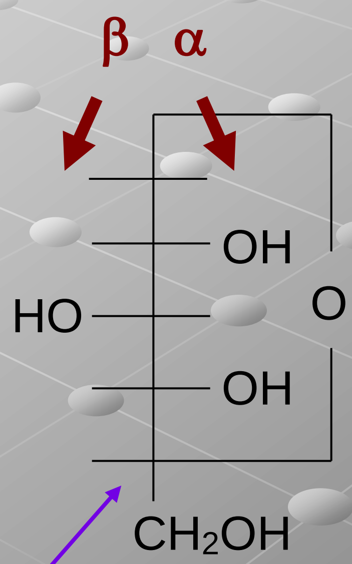
in an **α-sugar**, the –OH group is ***cis*** compared to the –OH group at the reference carbon atom*

in a **β-sugar**, the –OH group is ***trans*** compared to the –OH group at the reference carbon atom*

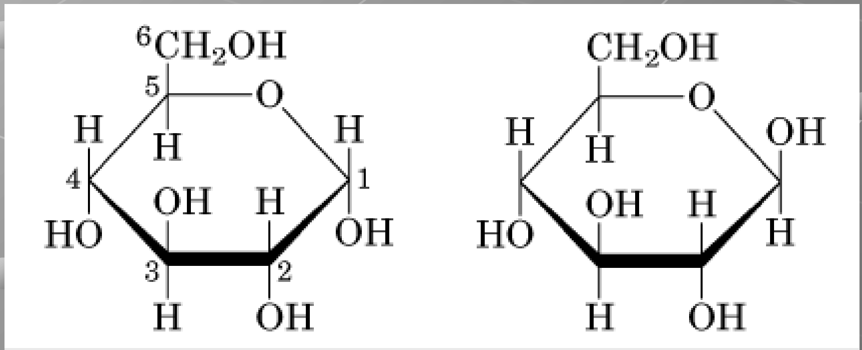
**Look back to the Fischer projection*:*

anomeric C-atom





reference C-atom



α,D-glucose β,D-glucose

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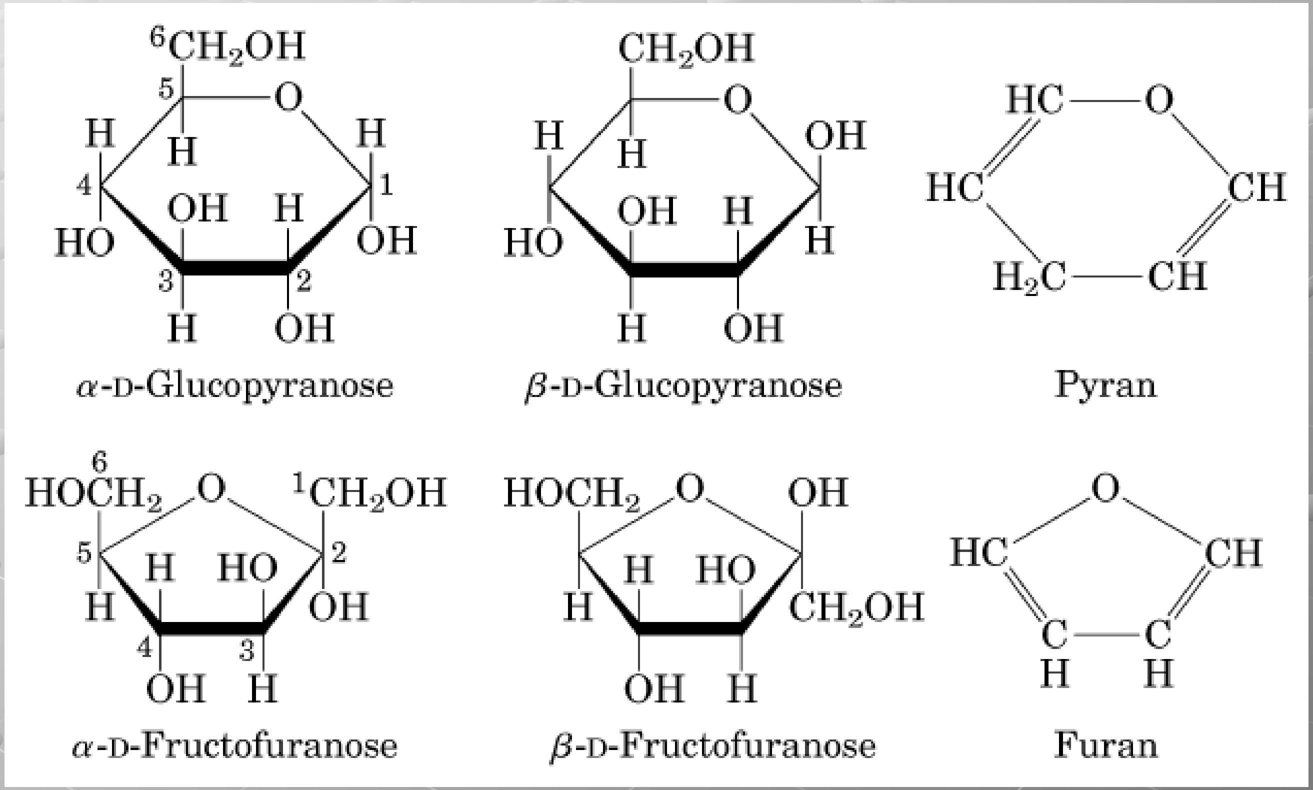
Sugar ring formation

Six-membered sugar rings are called *PYRANOSES*
Five-membered sugar rings are called *FURANOSES*



A six-membered aldopyranose ring is more stable than a five-membered aldofuranose ring, and thus predominates in an aldohexose solution

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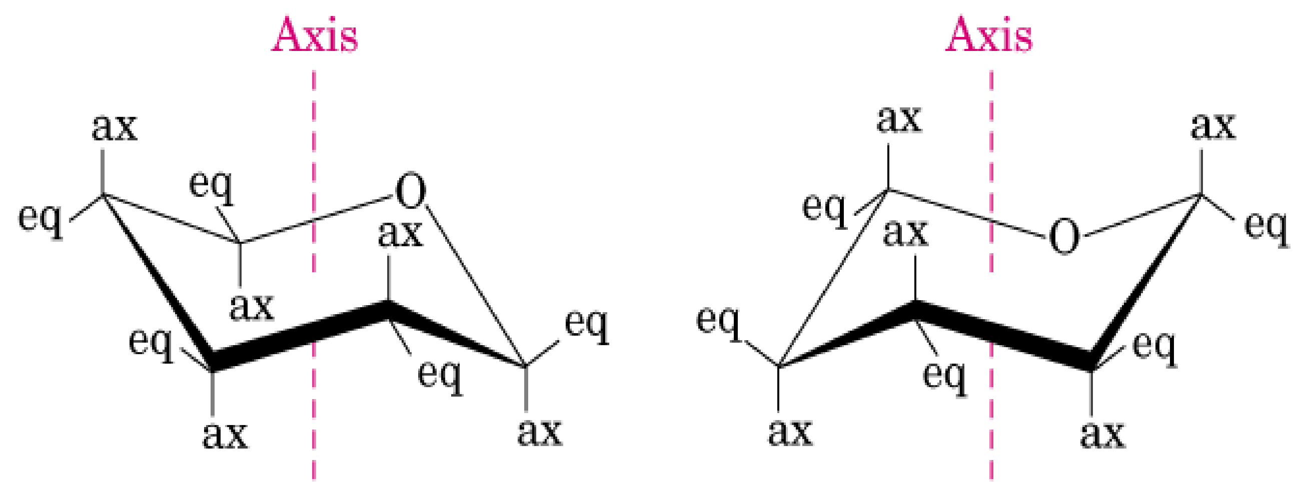
Is the Haworth saccharide projection a true representation of the real 3-D structure of the sugar?

NO, because sugar rings are not planar

A pyranose ring tends to adopt a "**chair**" conformation in solution



Two possible chair forms

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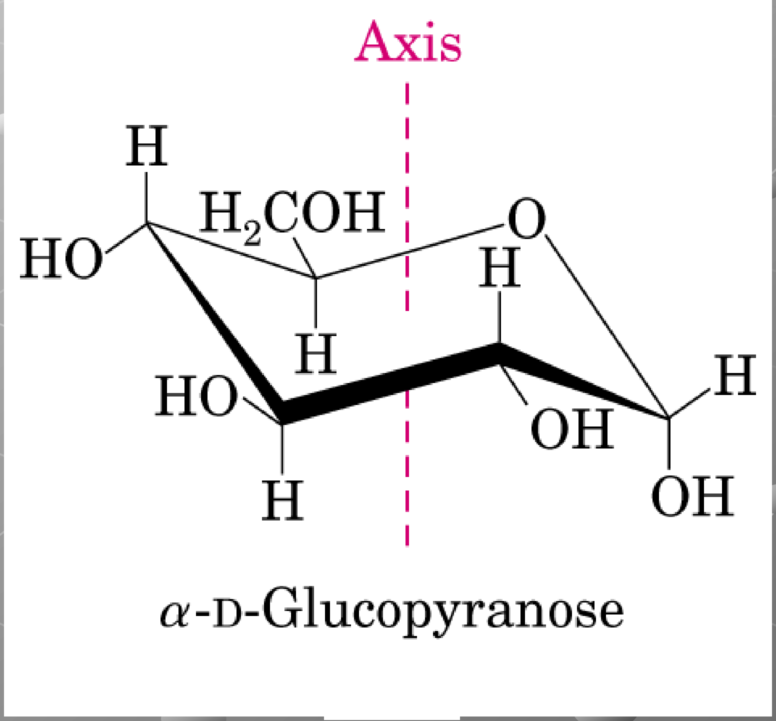
Substituents on the ring carbons may either be:
axial (ax, *i.e.* // with the vertical axis through the ring), or
equatorial (eq, *i.e.* projecting roughly ⊥ to this axis).

In general, substituents in equatorial positions are less sterically hindered by neighbouring substituents, and conformations with their bulky substituents in equatorial positions thus are favoured

A chair conformation of α-D-glucopyranose as an example



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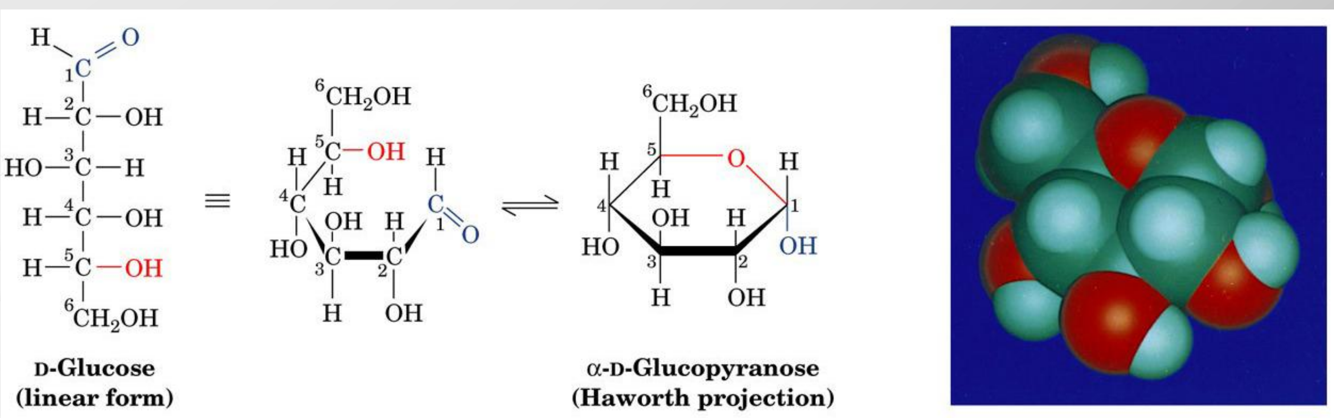
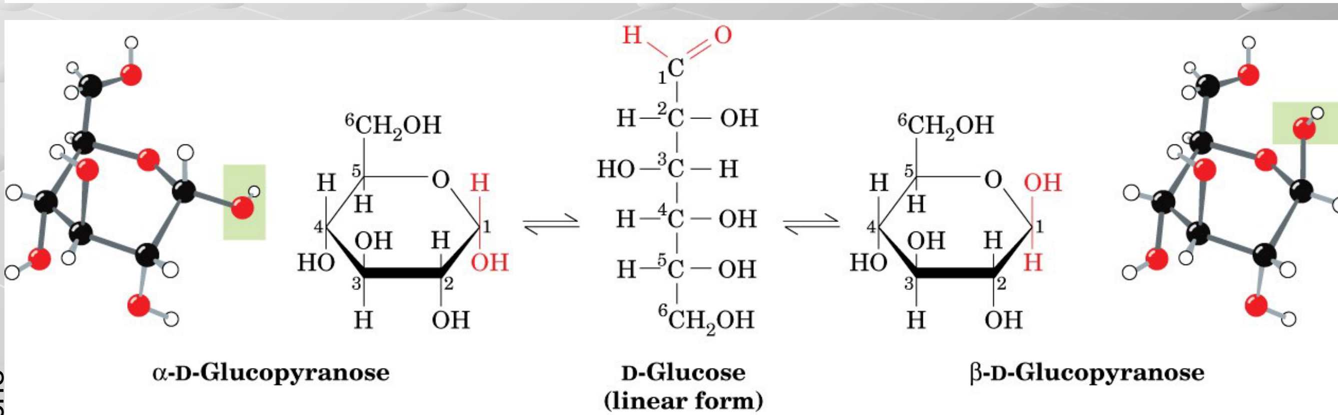
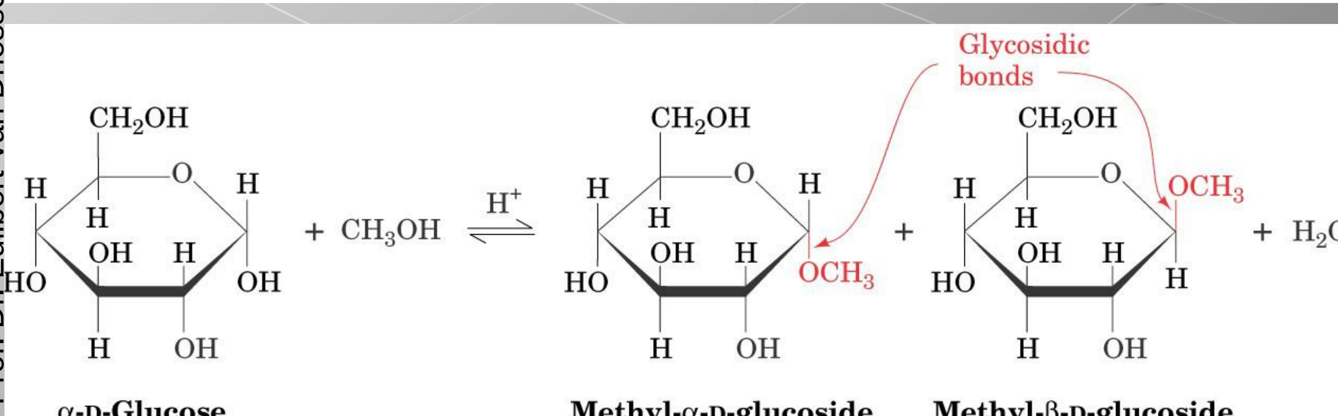
SUMMARY:



Monosaccharides form ring structures:
a pyranose is a 6-ring,
a furanose is a 5-ring.



The linear form is in equilibrium with two possible ring forms. Carbon C1 is called the anomeric carbon atom. If the –OH is below the ring, the linkage is called α; if the –OH is above the ring, it is called β.



When the hydroxyl group on the anomeric carbon atom is methylated, the two resulting molecules do not equilibrate anymore in solution.

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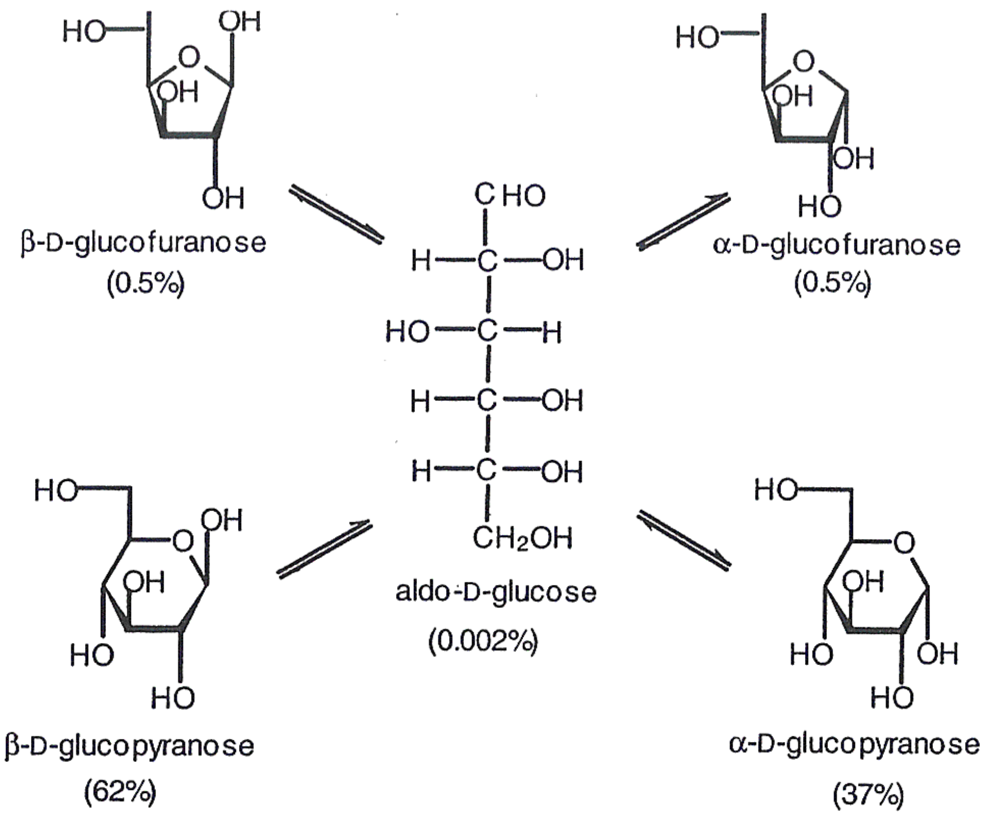
Mutarotation



Mutarotation gives the equilibrium mixture shown above, if the starting compound is any one of the five forms. The four ring structures are transformed into each of the other ring structures through the open chain form, until the equilibrium amounts are obtained.

The proces of mutarotation is slow, taking many hours to reach equilibrium in distilled water at 20°C. Both acid and base can catalyze the transformation.

Mutarotation

Distribution of α/β-Pyranose, α/β-Furanose, and Open-Chain Forms of Carbohydrates at Equilibrium in Water Solutions[a]

Carbohydrate	Temp. °C	Pyranose α	Pyranose β	Furanose α	Furanose β	Open-chain
D-Glucose	31	38.0%	62.0%	0.5%	0.5%	0.002%
D-Mannose	44	65.5%	34.5%	0.6%	0.3%	0.005%
D-Rhamnose	44	65.5%	34.5%	0.6%	0.3%	0.005%
D-Fructose	31	2.5%	65.0%	6.5%	25.0%	0.8%
D-Galactose	31	30.0%	64.0%	2.5%	3.5%	0.02%
D-Idose	31	38.5%	36.0%	11.5%	14.0%	0.20%
D-Xylose	31	36.5%	63.0%	0.3%	0.3%	0.002%
D-Ribose	31	21.5%	58.5%	6.4%	13.5%	0.05%

[a]Data from S. J. Angyal, *Adv. Carbohydr. Chem. Biochem.*, **42** (1984) 63–65.

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Decomposition of carbohydrates

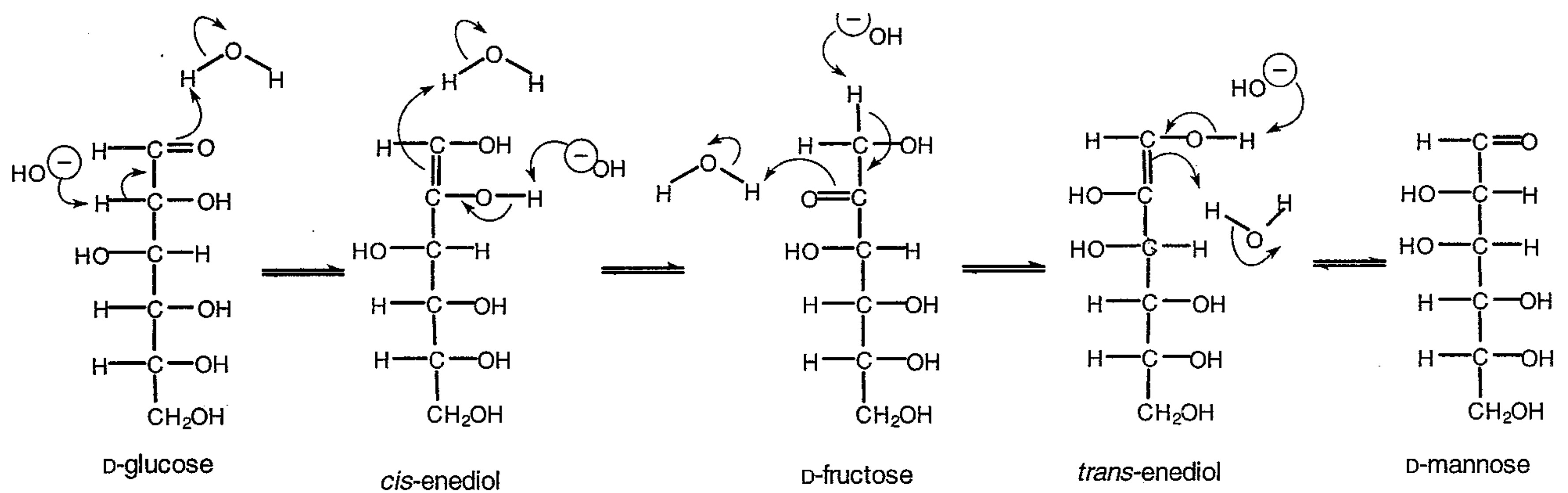
1. When sugars are heated to temperatures > 100°C, a complex series of reactions takes place. This process is known as **caramelisation** and results in a wide range of flavour compounds and brown pigments.
2. A related series of reactions known as **Maillard reactions** involves amino compounds.

1 & 2: non-enzymatic browning

The Lobry de Bruyn-Alberda van Eckenstein transformation

The first stage of the high temperature breakdown of sugars is a reversible isomerization of an aldose or ketose sugar via their open chain forms to an 1,2-enediol intermediate. These reactions result in epimerization of aldoses and ketoses, and aldose-ketose isomerization (first described by two Dutch chemists, Lobry de Bruyn and Alberda van Eckenstein).

Result: 2 epimers (glucose & mannose) and 1 ketose (fructose)



Lobry de Bruyn–Alberda van Eckenstein base-catalyzed isomerization.

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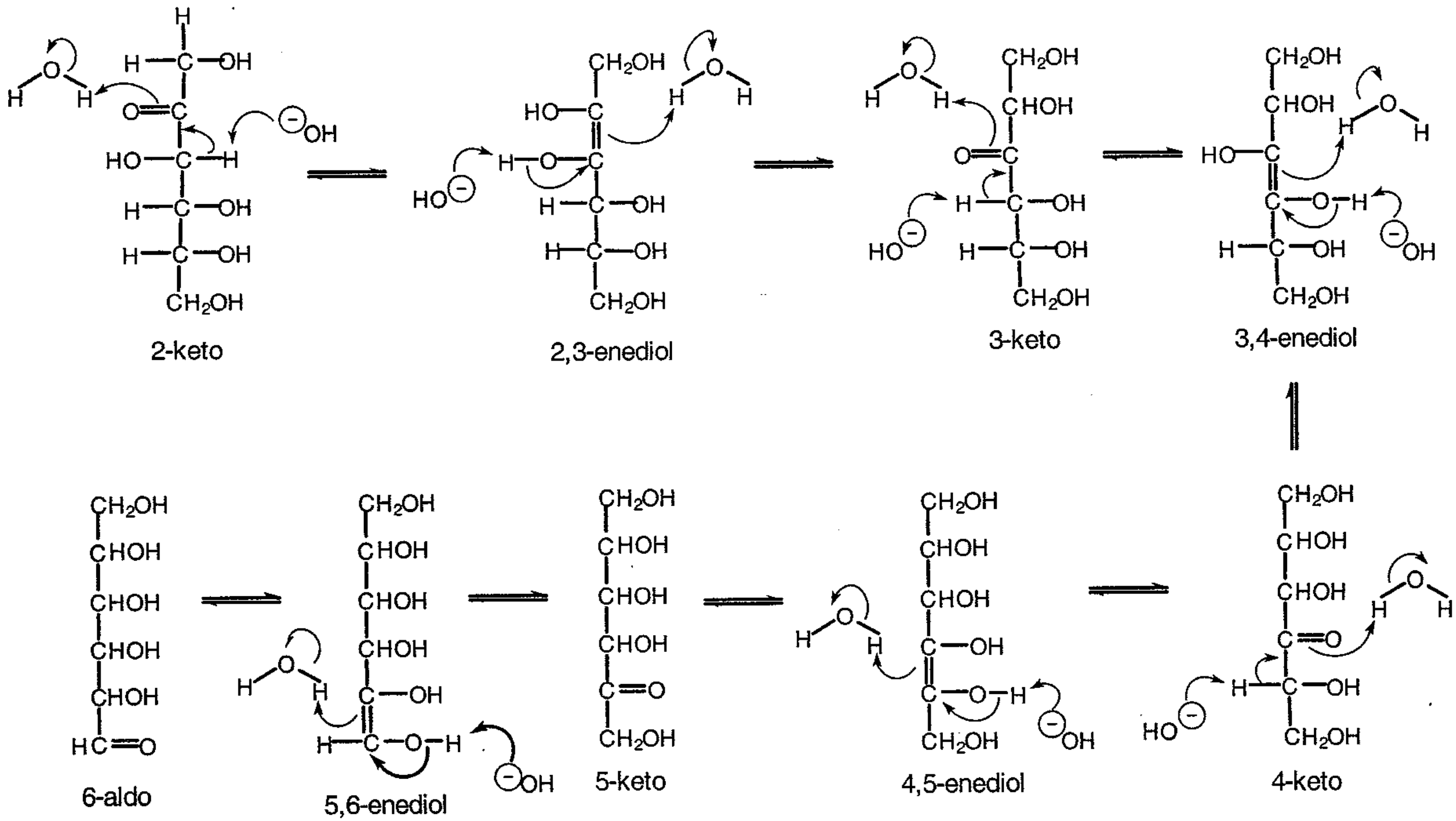
When pH is increased, the keto-enol isomerizations take place all along the carbohydrate chain



Lobry de Bruyn–Alberda van Eckenstein transformations at higher base concentrations and temperatures.

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Enzyme-catalyzed reactions that involve aldo-keto isomerizations of both phosphorylated and non-phosphorylated carbohydrates:

$$\text{D-glucose} \xrightleftharpoons[\textit{isomerase}]{\textit{glucose}} \text{D-fructose}$$

$$\text{D-xylose} \xrightleftharpoons[\textit{isomerase}]{\textit{xylose}} \text{D-xylulose}$$

$$\text{D-glucose-6-phosphate} \xrightleftharpoons[\textit{isomerase}]{\textit{phosphogluco}} \text{D-fructose-6-phosphate}$$

$$\text{3-phospho-D-glyceraldehyde} \xrightleftharpoons[\textit{isomerase}]{\textit{triosephosphate}} \text{dihydroxyacetone phosphate}$$

$$\text{D-ribose-5-phosphate} \xrightleftharpoons[\textit{isomerase}]{\textit{ribose-5-phosphate}} \text{D-ribulose-5-phosphate}$$

Glucose isomerase is used to convert high-glucose corn syrups into high-fructose corn syrups used as sweeting agents in soft drinks.

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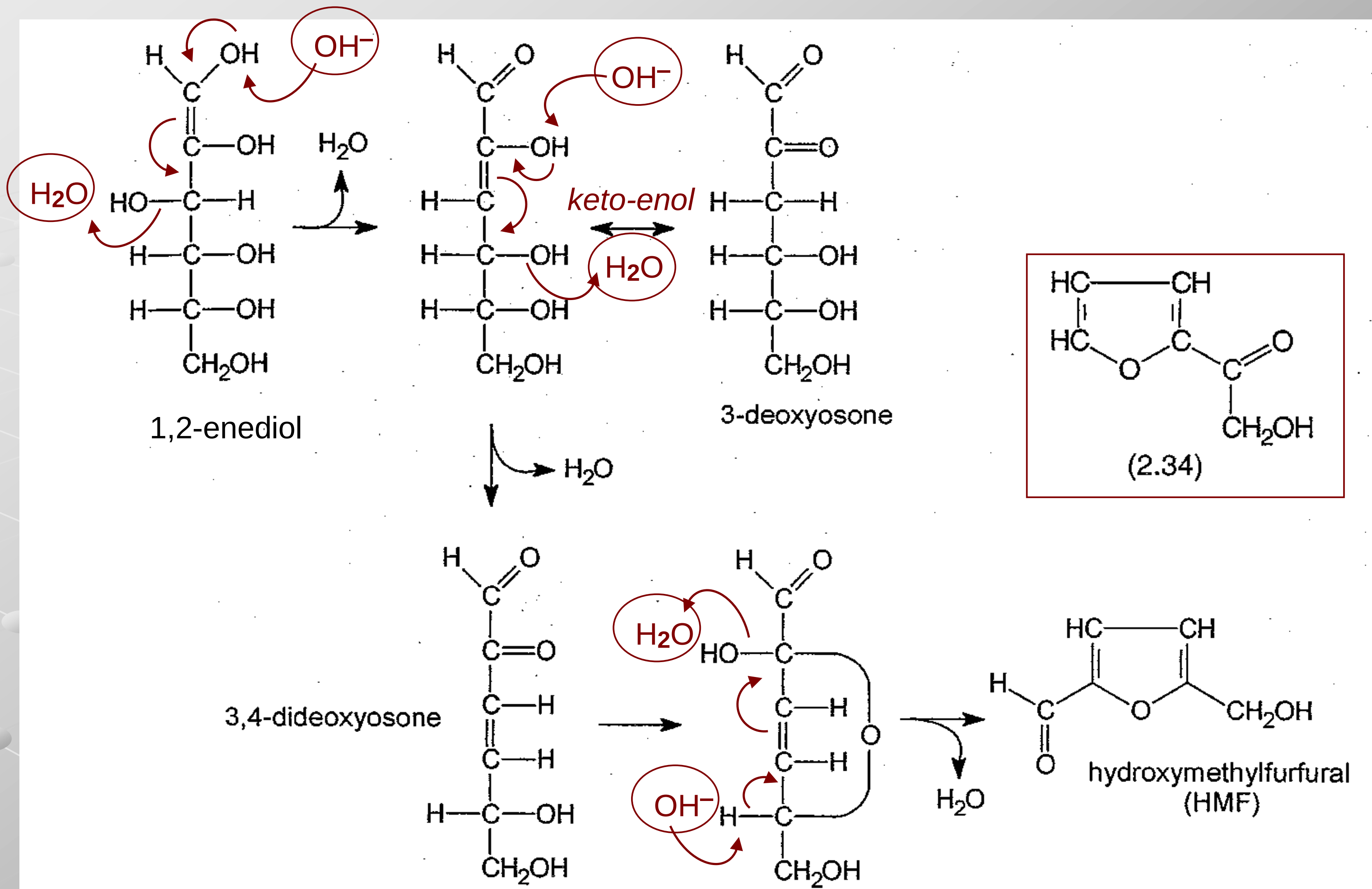
Dehydration of carbohydrates at high temperature



The formation of hydroxymethyl furfural by the sequential dehydration of a hexose enediol. Variations in the sites at which dehydration occurs is the source of related products such as hydroxyacetyl furan (2.34).

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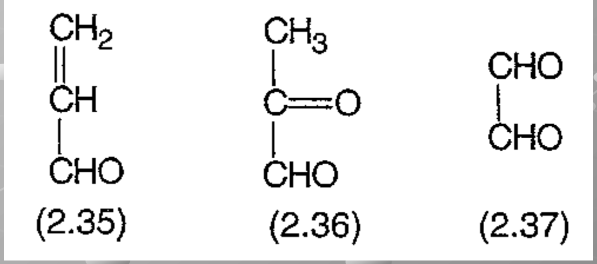
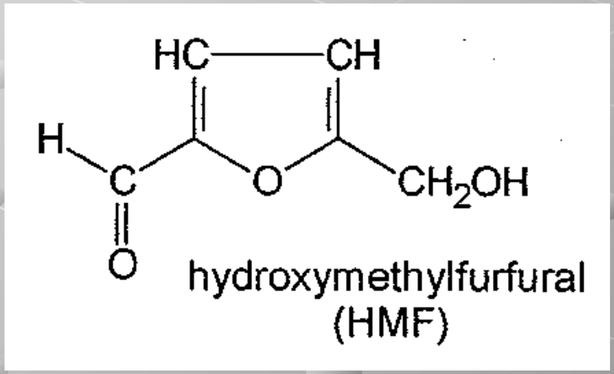
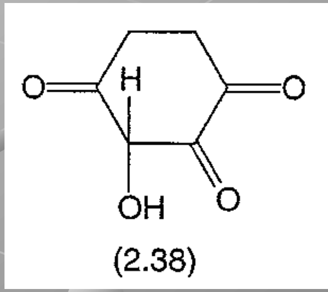
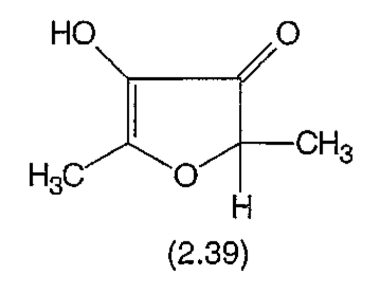
Some compounds formed upon heating carbohydrates (caramelisation)

Acrolein (2.35)
Pyruvaldehyde (2.36)
Glyoxal (2.37)
Acetylformoin (2.38)
4-Hydroxy-2,5-dimethylfuran-3-one (2.39)
Hydroxymethylfurfural









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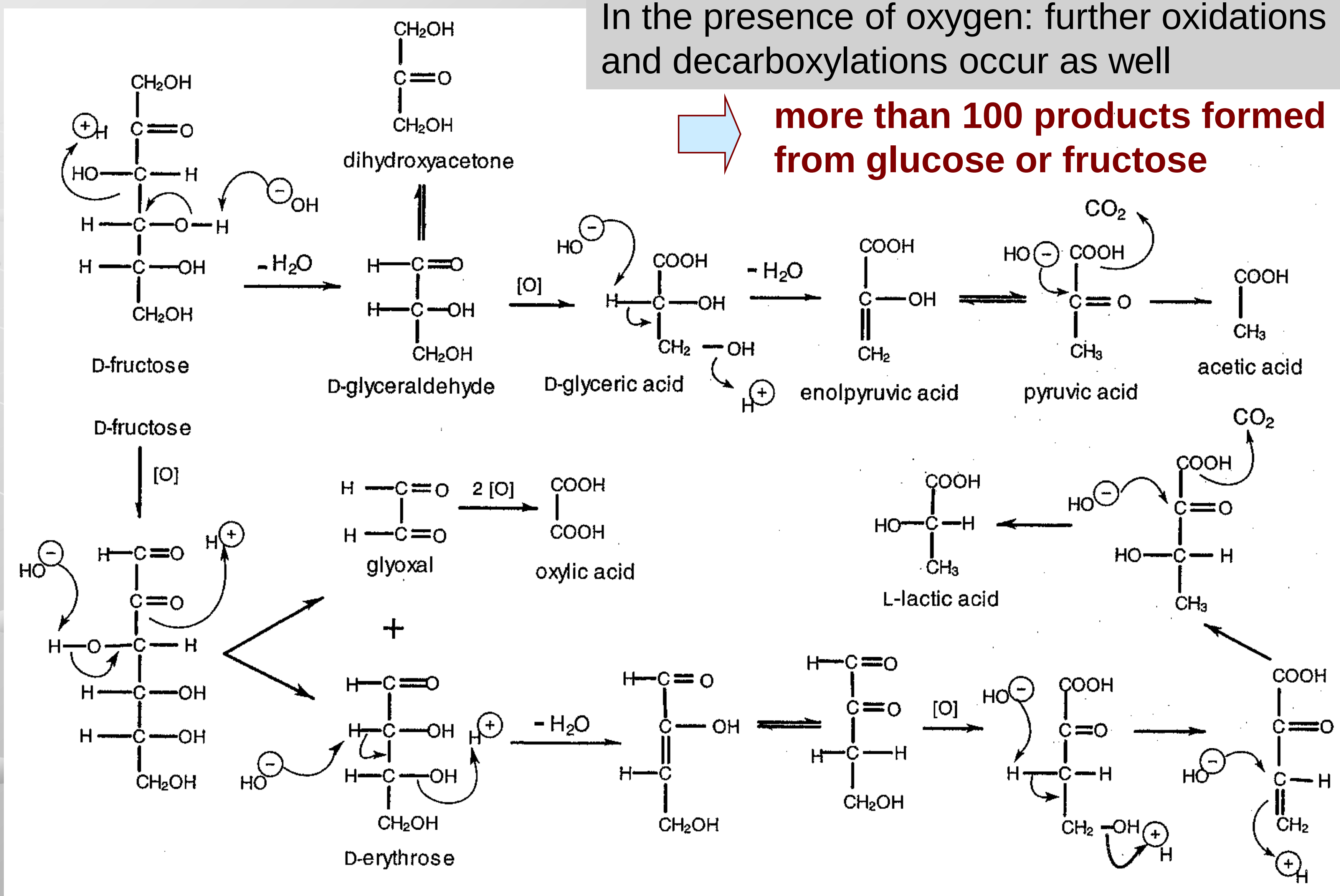
Alkaline oxidation and fragmentation reactions of carbohydrates at high temperature

In the presence of oxygen: further oxidations and decarboxylations occur as well

more than 100 products formed from glucose or fructose



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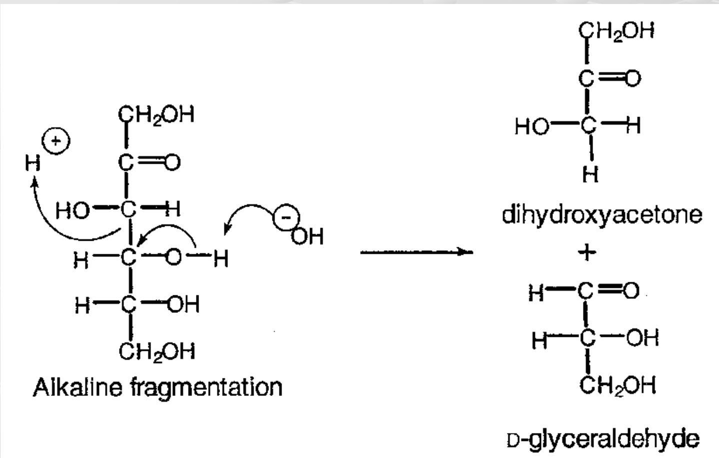
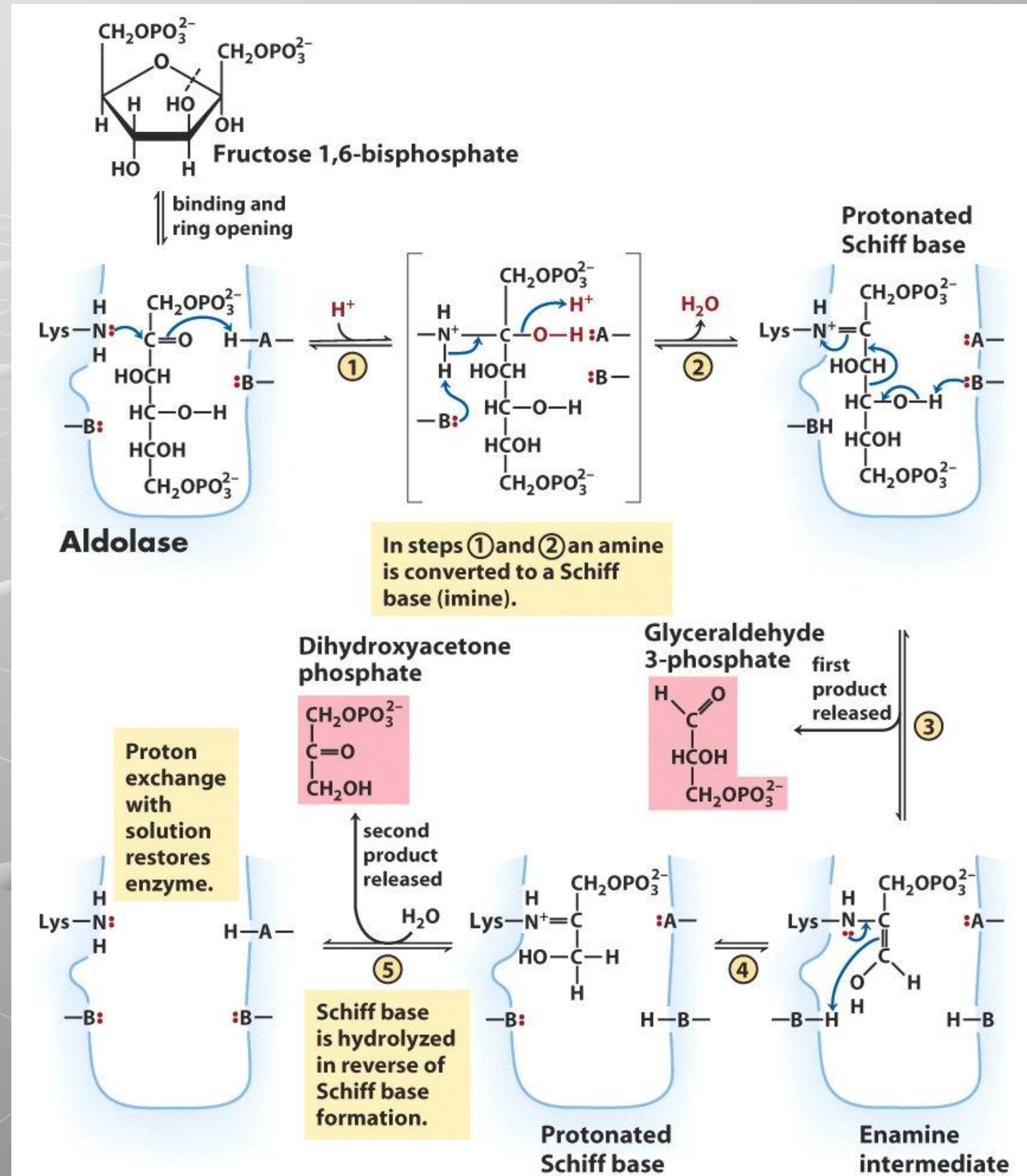
Mechanism for alkaline fragmentation of D-fructose:



… and fragmentation of D-fructose-1,6-bisphosphate by aldolase



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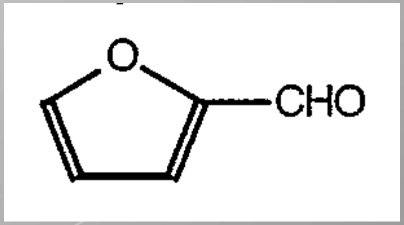
Reactions of carbohydrates with strong acid

Major reaction: dehydration
Major products formed: derivatives of furfural



aldohexoses	→	5-(hydroxymethyl)furfural
aldopentoses	→	furfural
6-deoxyaldoses	→	5-methylfurfural
aldohexuronic acids	→	5-carboxyfurfural

hexose
pentose $\xrightarrow{H^+}$ furfural or its derivatives

$- 3\ H_2O$

↓ *phenolic compounds*

coloured products

↓

colorimetric determination

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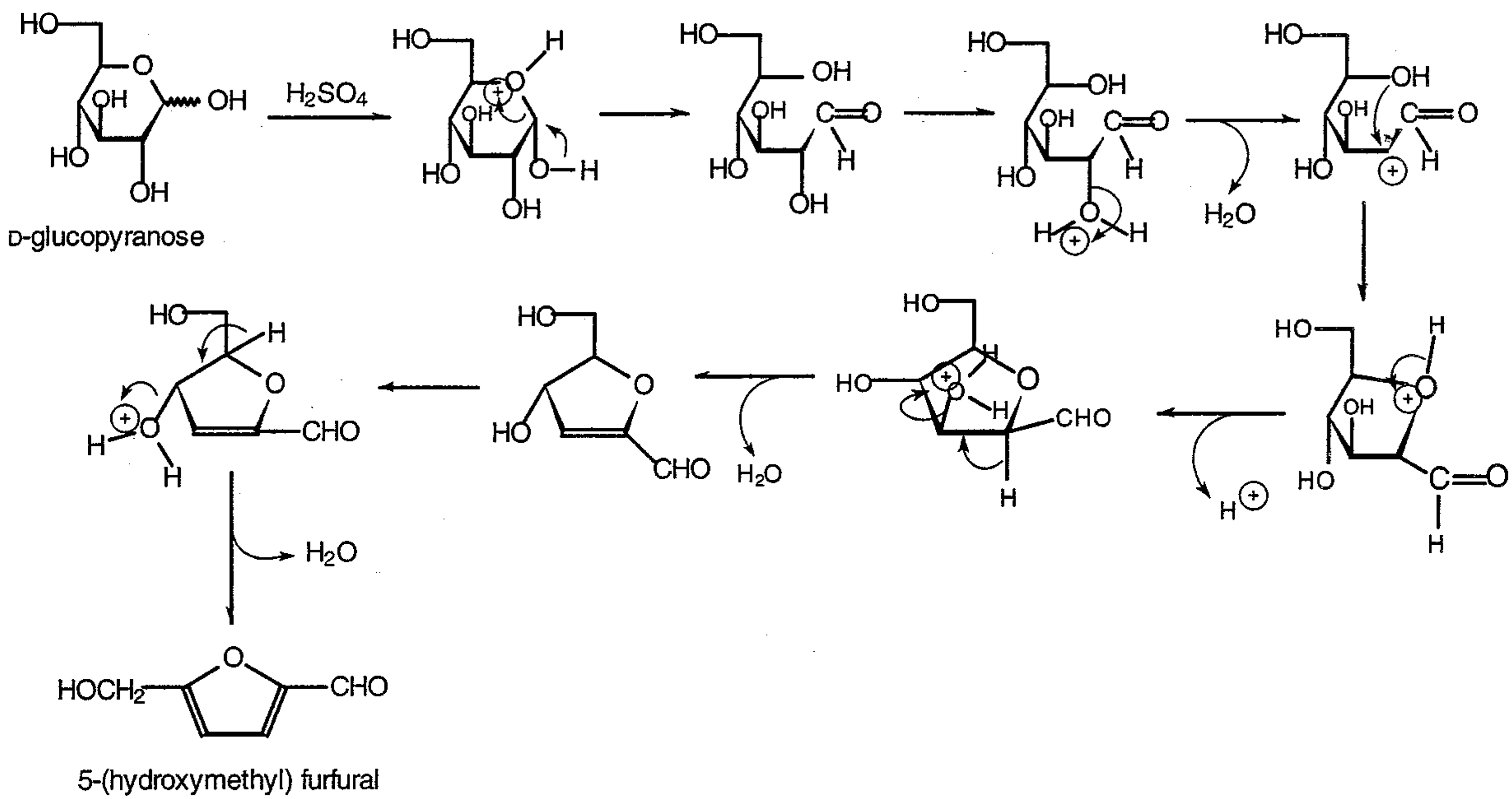
Dehydration of carbohydrates by strong acid



Mechanisms in the dehydration of carbohydrates by strong acid.

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The reaction of carbohydrates with concentrated sulfuric acid is used for the quantitative determination of carbohydrates present in solution

Table 3.2. Qualitative and Quantitative Determination of Carbohydrates with Strong Acid and Phenols

Name of test	Acid	Phenol	Carbohydrate determined	Type of test	Sensitivity	Color and absorbance
Molisch	H_2SO_4	α-Naphthol	All carbohydrates[a]	Qualitative	10 μg/mL	Purple
Anthrone	H_2SO_4	Anthrone	All carbohydrates[a]	Quantitative	50 μg/mL	Blue-green (600 nm)
Phenol sulfuric acid	H_2SO_4	Phenol	All carbohydrates[a]	Quantitative	10 μg/mL	Amber (470 nm)
Seliwanoff	HCl	Resorcinol	Ketoses	Qualitative	20 μg/mL	Red precipitate
Bial's	HCl	Orcinol	Pentoses[b]	Qual./quant.	20 μg/mL	Blue-green (600 nm)
Dische	H_2SO_4	Carbazole[c]	Uronic acids	Qual./quant.	10 μg/mL	Purple (535 nm)

[a]All carbohydrates except sugar alcohols, 2-amino and 2-acetamido, and 2-deoxy sugars.
[b]All pentoses except 2-deoxypentoses, which are dehydrated very slowly.
[c]Carbazole is an aromatic heterocyclic amine.

A number of colour reactions that are specific for carbohydrates depend on the formation of furfural derivatives in strong acid.

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Reducing reactions of carbohydrates

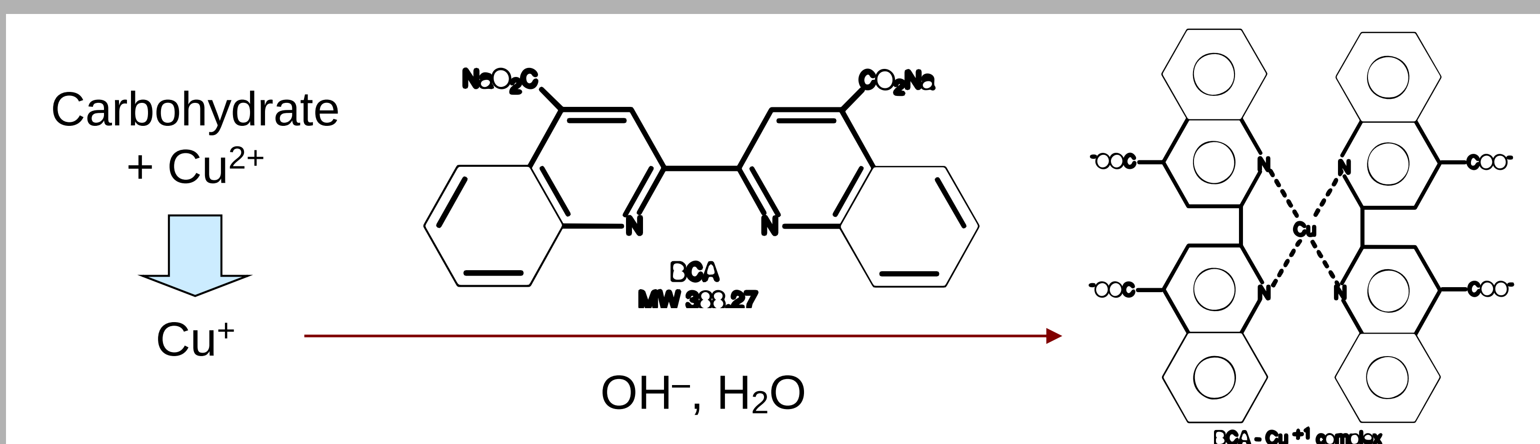
- Aldehydes in general reduce <u>Fehling's solution</u> (an alkaline solution containing a complex of copper tartrate) to red cuprous oxide:

  $$R\text{-}CHO + 2\,Cu^{2+} + 2\,OH^{-} \longrightarrow R\text{-}COOH + Cu_2O + 2\,H^{+}$$

  They also reduce <u>Tollens' reagent</u> (ammoniacal silver nitrate solution) to metallic silver, appearing as a silver mirror.
  In both cases the aldehyde is oxidised to the corresponding acid:

  $$R\text{-}CHO \longrightarrow R\text{-}COOH$$

- Reducing sugars react with Cu^{2+} producing Cu^{+}. Cu^{+} is chelated by BCA (<u>bicinchoninic acid</u>), which converts the greenish colour of the BCA to the purple colour of the Cu^{+}-BCA complex. The absorbance is read at or near 562nm.



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Reducing reactions of carbohydrates

- Enzymes are also used in the oxidation of carbohydrates as a means of determining specific sugars, *e.g*. β-D-glucopyranose is very specifically oxidized to D-gluco-1,5-lactone by glucose oxidase:

$$\text{D-glucose} \xrightarrow[\text{mutarotase}]{\textit{glucose oxidase}} \text{D-glucono-1,5-lactone} + H_2O_2$$

$$H_2O_2 \xrightarrow{\textit{peroxidase}} O_2 + H_2O$$

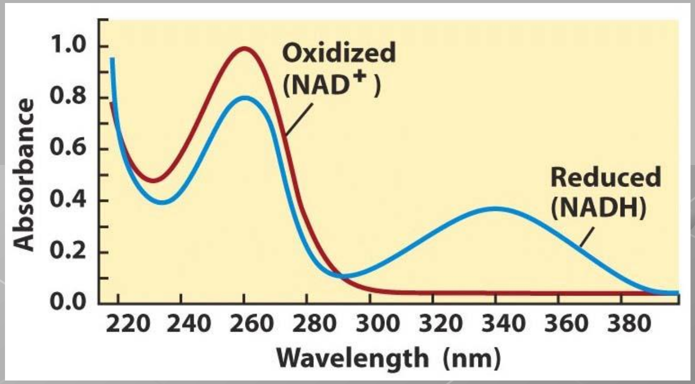
$$O_2 + H_2O \xrightarrow{o\text{-dianisidine}} \text{purple colour measured at 525nm}$$

- Alternatively, glucose is also measured by D-glucose-6-phosphate dehydrogenase:

$$\text{D-glucose} \xrightarrow[\text{ATP}]{\textit{hexokinase}} \text{D-glucose-6-phosphate}$$

$$\text{D-glucose-6-phosphate} \xrightarrow[NADP^+]{\textit{glucose-6-P-dehydrogenase}} \text{NADPH} + \text{6-phospho-1,5-D-gluconolactone}$$

NADPH measured at 320nm



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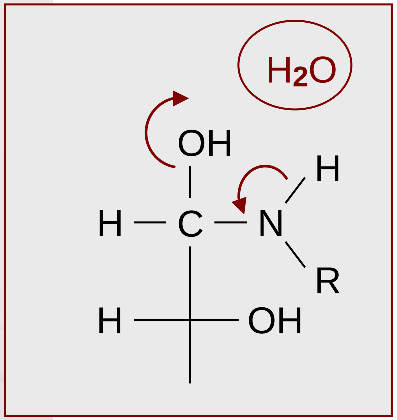
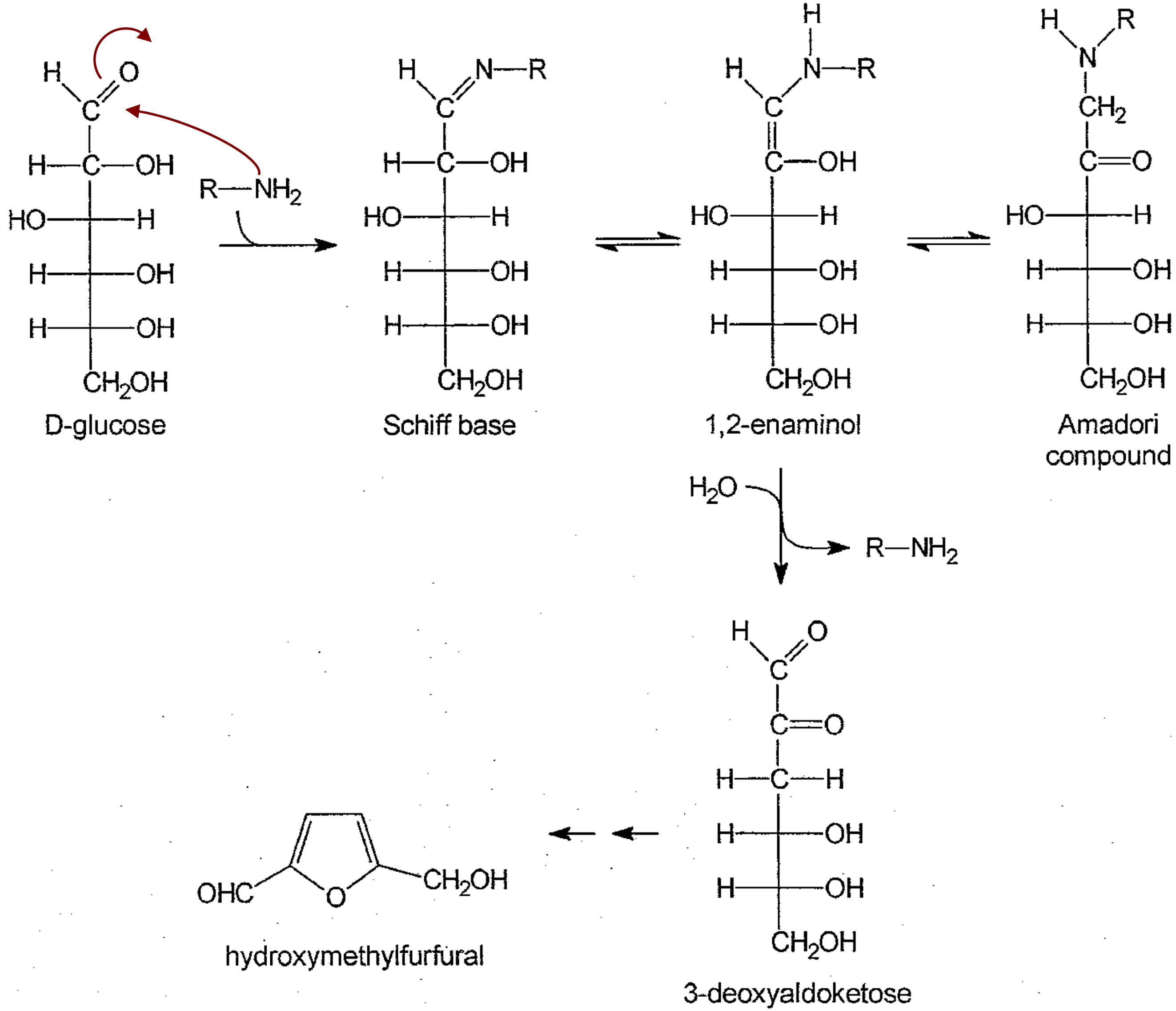
Reactions of carbohydrates with amino compounds: the Maillard reaction

Non-enzymatic browning is caused by what is known as the Maillard reaction

→ Formation of N-glycosides + numerous other products including brown pigments

- N-glycosides result from the reaction between reducing sugars and proteins, peptides, amino acids and amines
- N-glycosides are more readily formed at higher temperature, low water activity and upon storage
- Major sugars involved: glucose, fructose, maltose, lactose and to some extent reducing pentoses such as ribose
- Major amino acids involved: those with a primary amino group because their content is higher in food than those with a secondary amino group
- In proteins: mainly lysine (because of its ε-amino group); also arginine reacts with dicarbonyl compounds
- Reactions are similar to those in acid/base catalyzed conversions of monosaccharides, but the Maillard reactions proceed under much milder conditions as those present in food





The formation of hydroxymethyl furfural (HMF) in the Maillard reaction. R-NH_2 *can be any compound with a free amino group as discussed in the text. The dehydration and cyclisation reactions of 3-deoxyaldoketose (often referred to as 3-deoxyhexulose or 3-deoxyosone) to give (HMF) are exactly the same as those in caramelisation*

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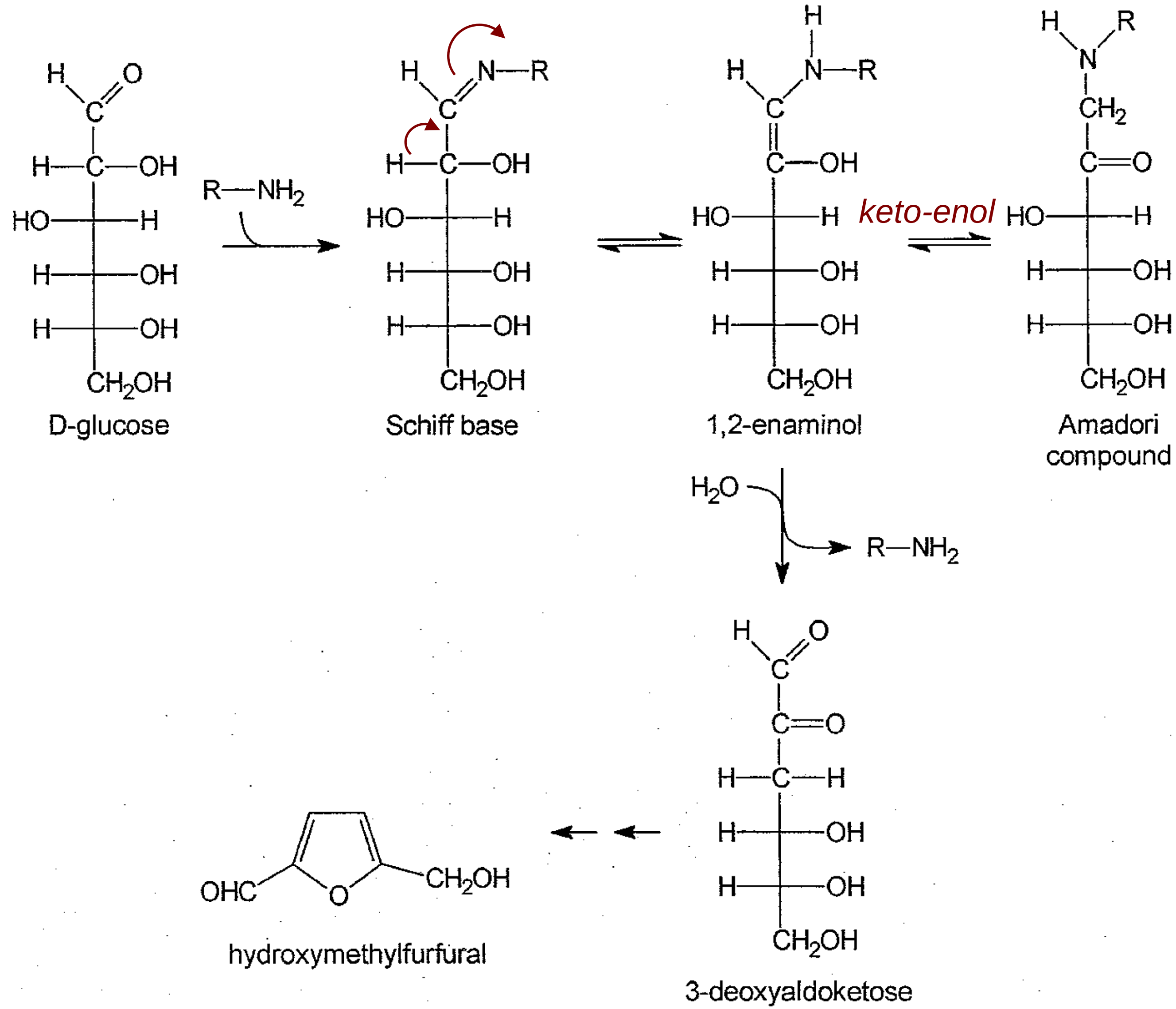

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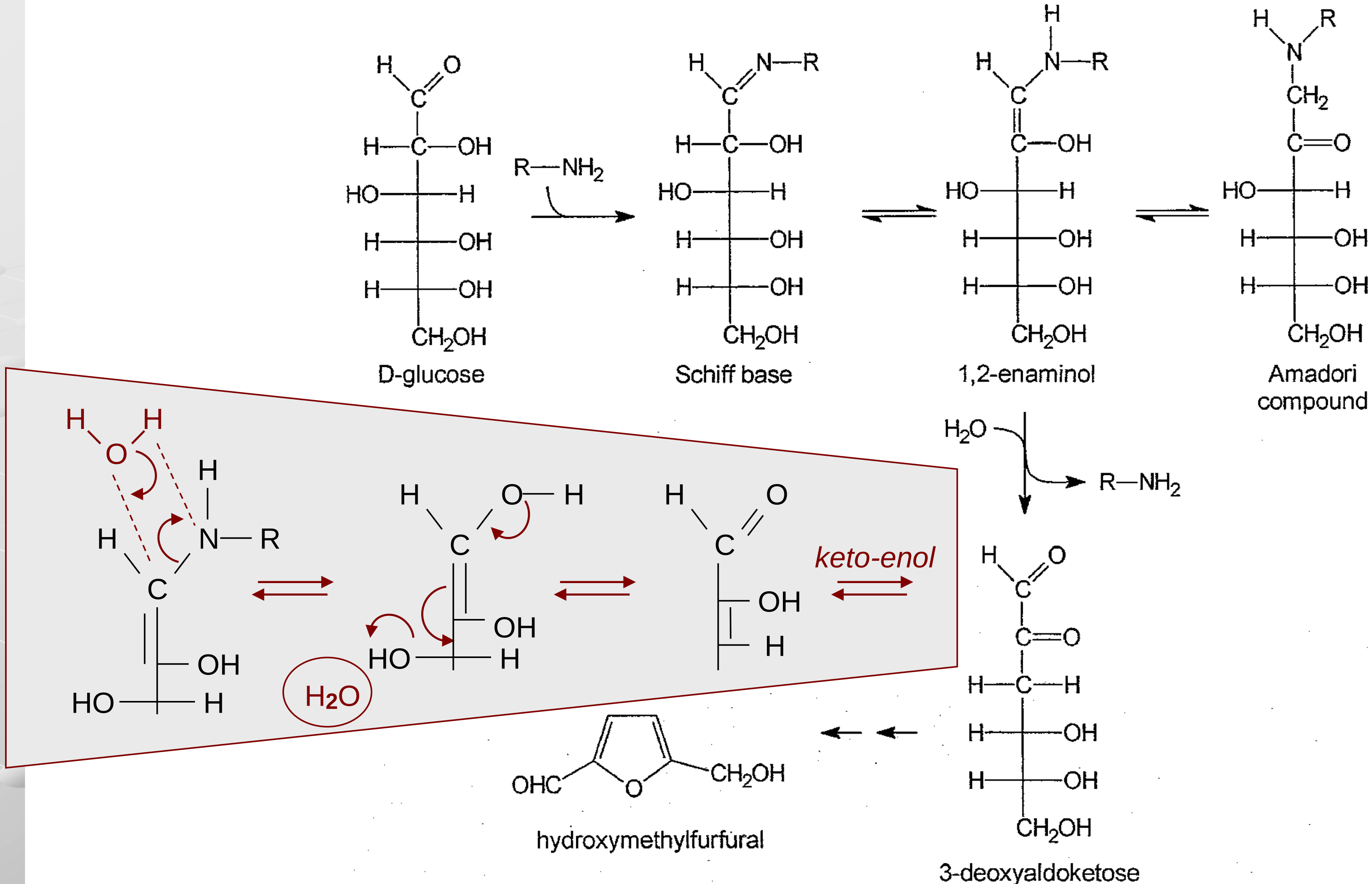

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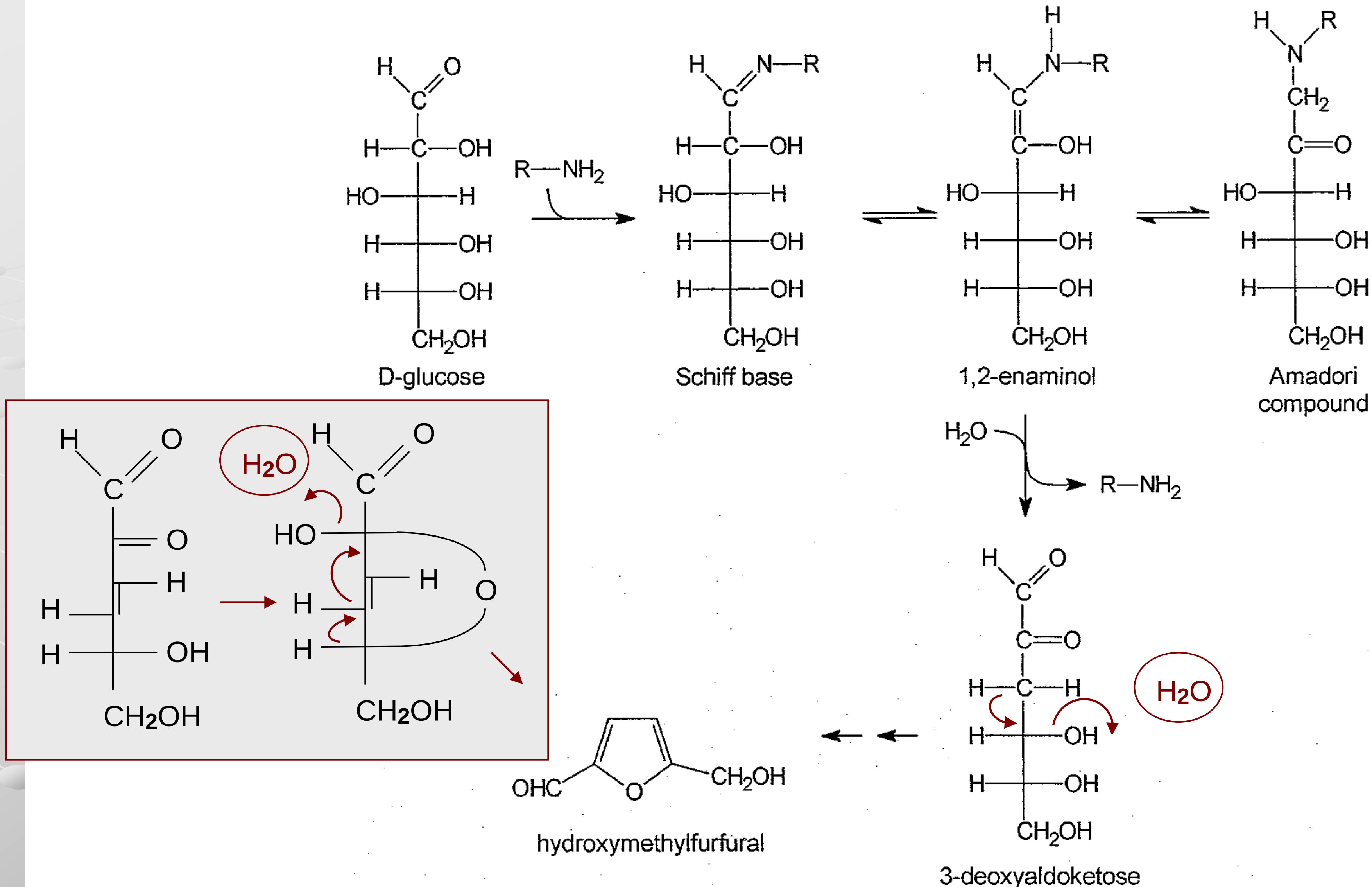

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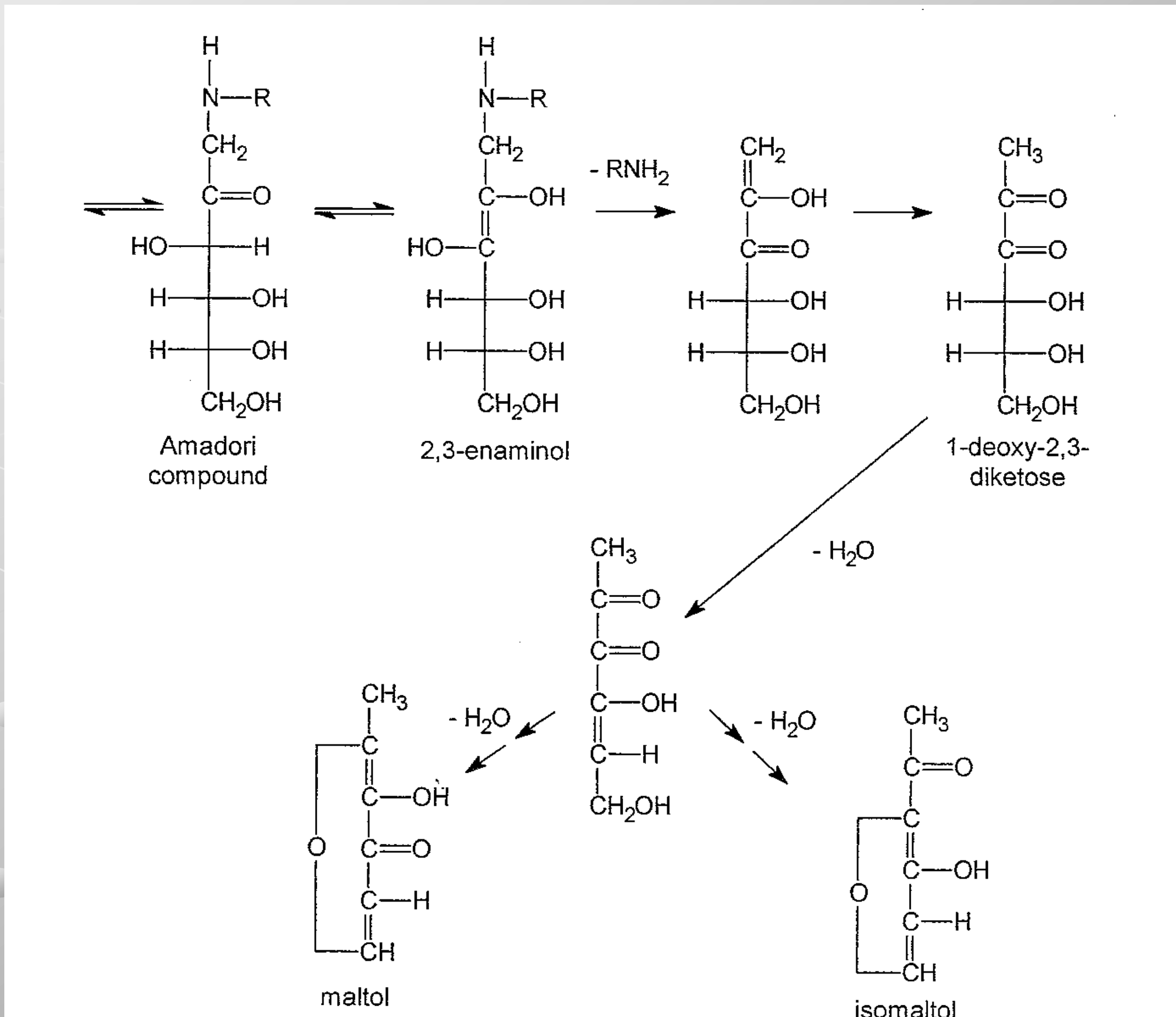
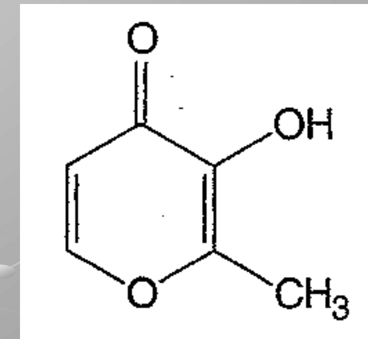
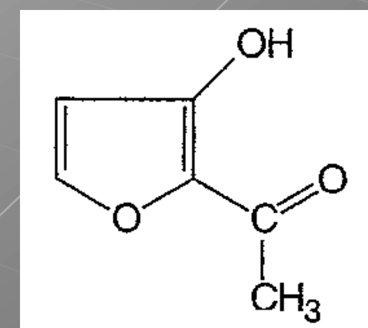
Formation of maltol and isomaltol from Amadori compounds formed in the Maillard reaction





maltol



isomaltol

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Inhibition of Maillard reactions

In cases where Maillard reactions are undesirable, they can be inhibited by:

- Lowering the pH
- Maintaining the lowest possible temperature
- Avoiding critical water contents. Keeping the water activity of dried products as low as possible
- Use of non-reducing sugars or elimination of reducing sugars by *e.g*. fermentation or enzymatic treatment
- Blocking with *e.g*. bisulfite at low concentration

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Effects of Maillard reactions: both desirable and undesirable

- Formation of brown pigments, *i.e*. melanoidins (a highly heterogeneous group of nitrogen-containing pigments)
  - Desired: backing and roasting of meat
  - Non-desired: browning of fish, condensed milk, white dried soups, *etc*.
- Formation of volatile compounds that contribute to the aroma formation during cooking, backing, roasting or frying. However, some compounds provoke off-flavors during storage, especially in dehydrated state or upon heating (pasteurization, sterilization, roasting)
- Formation of bitter substances during roasting (coffee). Some give off-taste to meat and fish
- Formation of compounds with highly reductive properties (reductones) that protect food against deterioration
- Losses of essential amino acids (K, R, M, C)
- Formation of compounds that are potentially carcinogenic
- Formation of compounds that cause cross-linking of proteins
  – in diabetic patients: sight-loss (retinopathy), degradation of the peripheral vascular system

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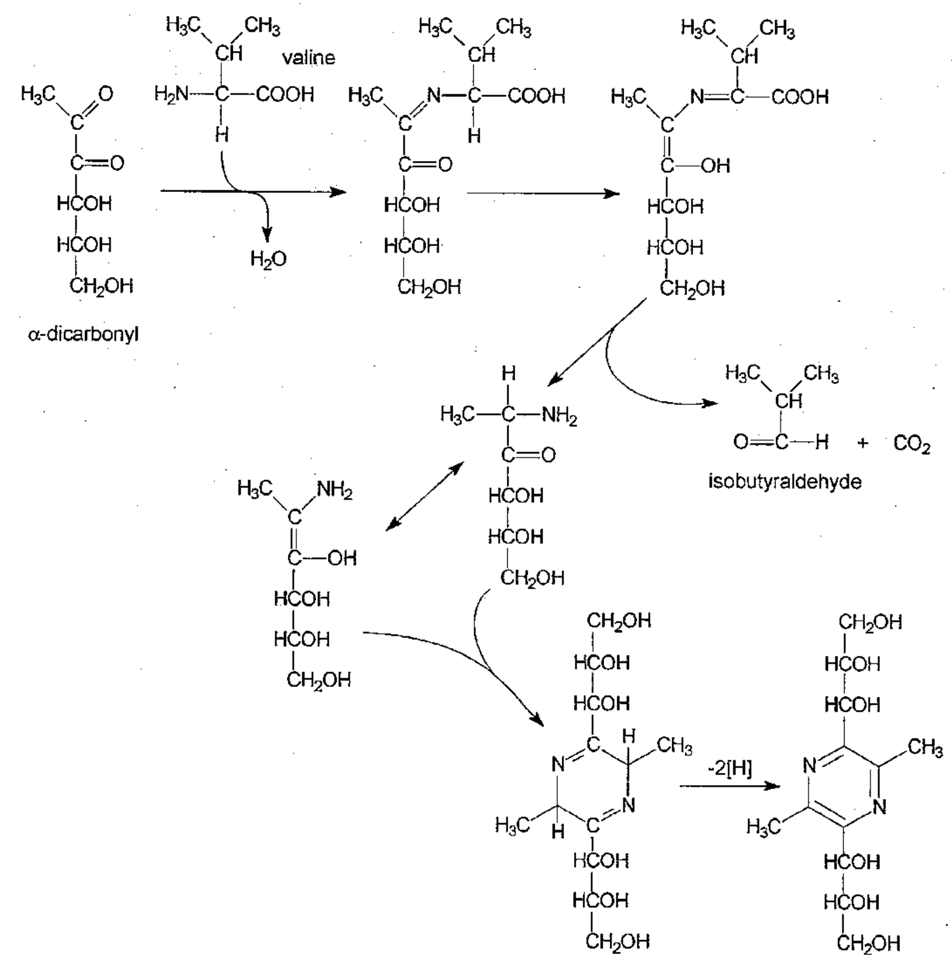
Strecker degradation: reaction of free amino acids with dicarbonyl compounds generated in the Maillard reaction

- Formation of volatile flavour compounds (volatile aldehydes) at high temperature by interaction of dicarbonyl compounds with α-amino acids
- Volatile aldehydes give attractive odour to bread, cake, bisquits
- Pyrazines contribute to the flavour of chocolate and roasted meat



The Strecker degradation. A free amino acid (in this case illustrated by valine) reacts with an α-dicarbonyl compound generated elsewhere in the Maillard reaction. The reactions bears a superficial resemblance to transamination (see Figure 8.2). After rearrangement the carbon skeleton of the amino acid is liberated as a volatile aldehyde. After two ex-sugar fragments (not necessarily, as shown here, identical) condense the product is readily oxidised to give the pyrazine derivative.

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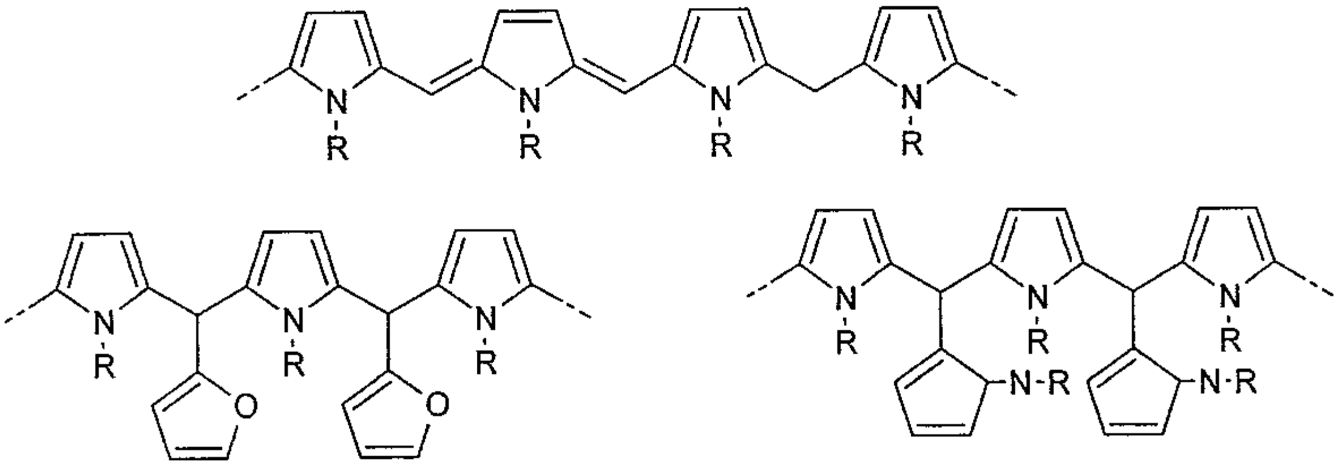
Brown mellanoidin pigments formed in the Maillard reaction



Postulated structures for the brown, melanoidin pigments formed in the Maillard reaction. In these structures R *represents any of the possible sugar fragments such as* $-CH_3$, $-(CHOH)_2CH_2OH$, *etc. that arise during the course of the reaction. All of the structures shown here are likely to found in a single melanoidin molecule. It has been estimated that around 95% of molecules initially participating in the Maillard reaction eventually end up in melanoidin polymers.*

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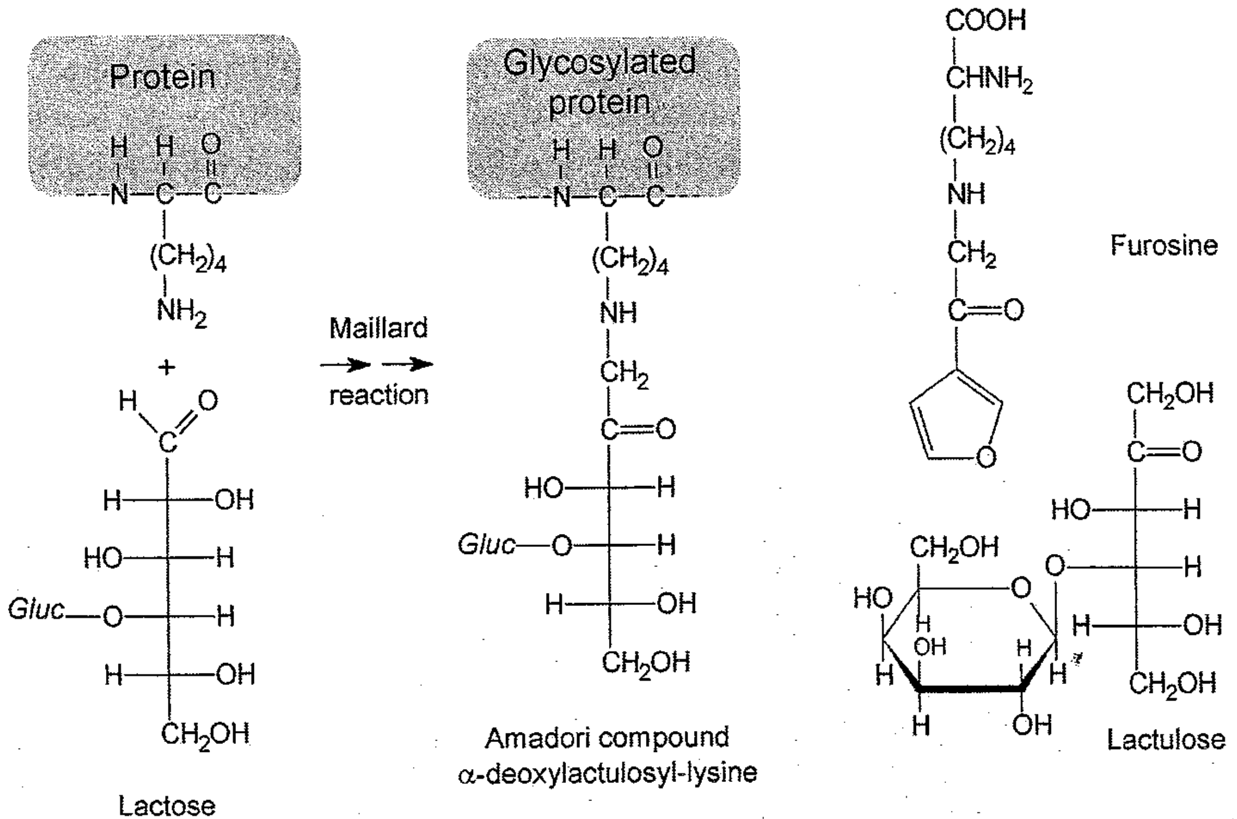
Non-enzymatic browning of food proteins



Lactose reactions during milk processing. The extent of glycosylation in a food protein can be estimated from the furosine content of the hydrolysate after it has been subjected to acid hydrolysis. Also at high temperatures small amounts of lactose undergo the Lobry de Bruyn–Alberda van Eckerstein transformation (see Figure 2.8) to give lactulose, i.e. *the glucose component of the disaccharide is converted from glucose to fructose, shown here for clarity in the 'open-chain' structure. Measurements of furosine and lactulose levels are becoming important in establishing the processing history of commercial milk products.*

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Non-enzymatic browning of food proteins

- Glycosylation of proteins can interfere with their digestibility by proteolytic enzymes
- Especialy reactive amino acids: K, W, H (all essential amino acids)
  Examples: -pasteurization of milk gives 2% lysine loss
  -sterilization, evaporation, or roller-drying results into about 25% lysine loss
- A mixture of glucose and casein loses 70% of lysine over a period of 5 days at 37°C
  Problem: transport of milk powder in tropics to areas of famine!

Non-enzymatic browning in diabetes mellitus

- Normally, 3-7% of hemoglobin is glycosylated (formation of HbA1C)
- In diabetis patients, HbA1C is much higher
- Long term effects: retinopathy, degeneration of the peripheral vascular system; kidney failure

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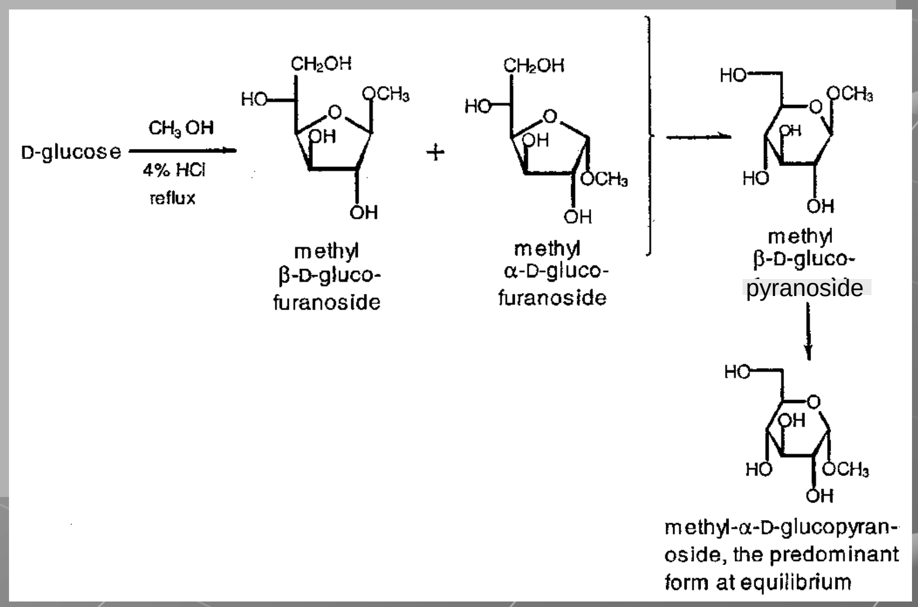
Reactions of hemiacetals or hemiketals with alcohols

- The most reactive hydroxyl group of a carbohydrate is the hemiacetal or hemiketal hydroxyl group that is formed when cyclic furanose or pyranose rings are formed (i.e. the –OH group on the anomeric carbon atom).
- These hydroxyls can react with alkyl and aralkyl alcohols and with aryl phenols to split out water and give a glycoside.
- The alkyl, aralkyl or aryl group is called the aglicone group, while the sugar residue is called the glycosyl group.
- Glycosides can be glycopyranosides or glycofuranosides and they can have an α- or β-configuration.
- They are synthesized by the Fischer method starting mostly from a mono-saccharide. The furanose form of the sugar reacts most rapidly.
- The α-D-pyranoside is the predominant product due to the anomeric effect



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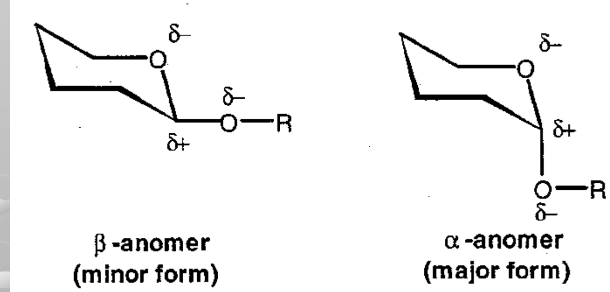
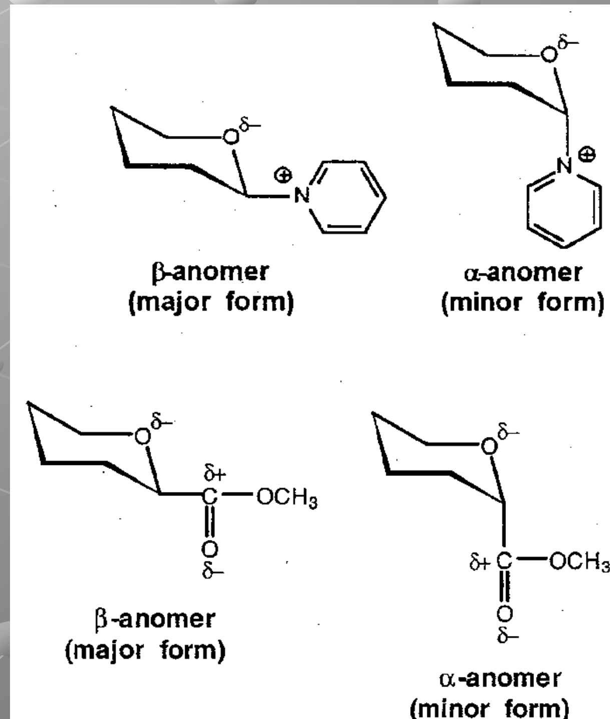
The anomeric effect

- The formation of α-D-pyranoside as the predominant product is interpreted as due to the phenomenon called “the anomeric effect”.
- The reverse “anomeric effect” occurs when an atom from the aglycone attached to C-1 has a positive or partially positive charge.



Anomeric Effect

- Glycosides are non-reducing because it is no longer possible to form free aldehyde or ketone.
- *In vivo*, glycosidic linkages between two or more saccharides are formed by specific enzymes (see glycogen and starch bio-synthesis, and biosynthesis of glycoproteins).



Reverse Anomeric Effect

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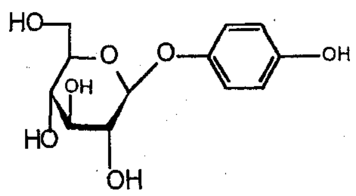
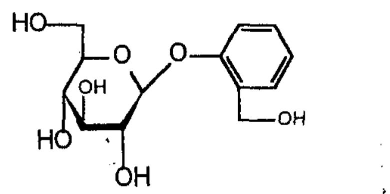
Some biological effects of glycosides

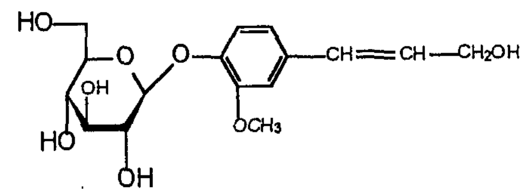
Naturally occurring glycosides are mainly found in plants and some have medicinal effects, while others are poisonous:



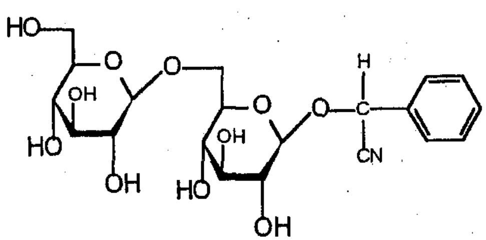
Arbutin is found in the leaves of blueberries, cranberries, and pear tree. It has been used as a diuretic and anti-infective urinary agent.



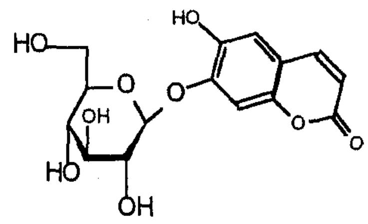
Salicin is found in the bark of willow and poplar. It has been used as an analgesic agent.



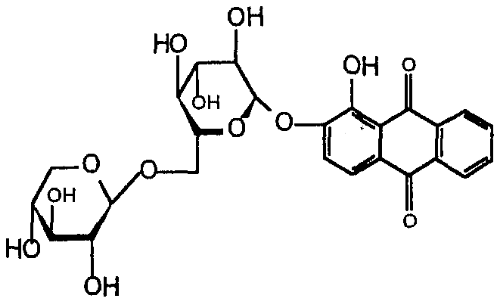
Coniferin is found throughout the *Gymnospermae*. The aglycone is the monomer of lignin and the glycoside may be the precursor to lignin biosynthesis. It is alsofound in comfrey root, sugar beets, and asparagus.



Amygdalin occurs in the seeds of Rosaceae -- bitter almonds, peach, and apricot seeds. It has been suggested as an anti-cancer drug, and has been used in some countries to treat cancers. There, however, is no hard data to substantiate its *effectiveness* in such treatments.



Aesculin is found in the leaves and bark of the horse chestnut. It is used as a skin protectant in sun-tanning preparations.

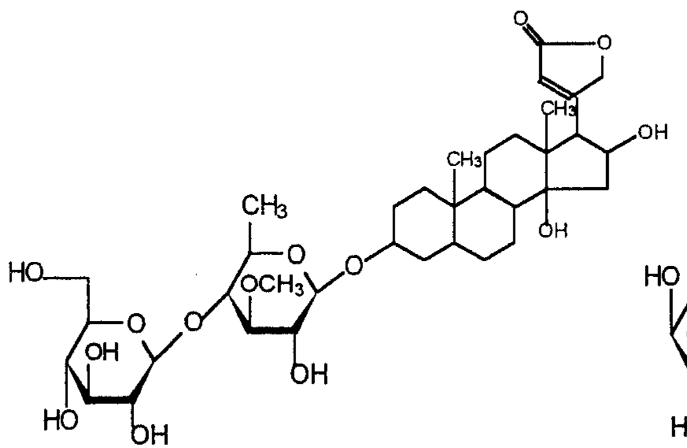


Ruberythric acid is an anthraquinone glycoside found in the madder root. The aglycone is alizarin, which is used in dyeing and staining. The carbohydrate is a disaccharide of β-D-xylopyranose linked 1,6 to β-D-glucopyranose, which is called *primeverose*.

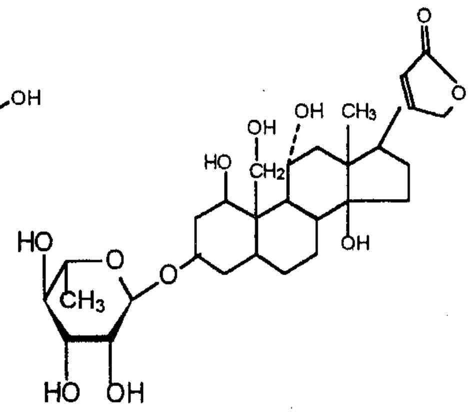
Glycosides found in plants, and their sources and uses.

Some biological effects of glycosides

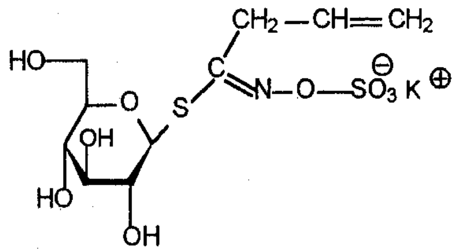
Naturally occurring glycosides are mainly found in plants and some have medicinal effects, while others are poisonous:



Digitalin is obtained from the seeds of *Digitalis purpure*. The aglycone is a steroid attached to a disaccharide of β-D-glucopyranose attached to 3-O-methyl-D-quinovose (3-O-methyl-6-deoxy-D-glucose). It is a powerful cardiac stimulant.



Ouabain is a cardiac glycoside (used as an arrow poison). Even though it is a toxic glycoside, it is used in low concentrations as a heart stimulant. The carbohydrate is α-L-rhamnose.



Sinigrin and analogous glycosides are found throughout the *Crucifera*. It is commonly isolated from black mustard seeds and from horseradish root. It is believed to contribute to the hot flavor of these materials.

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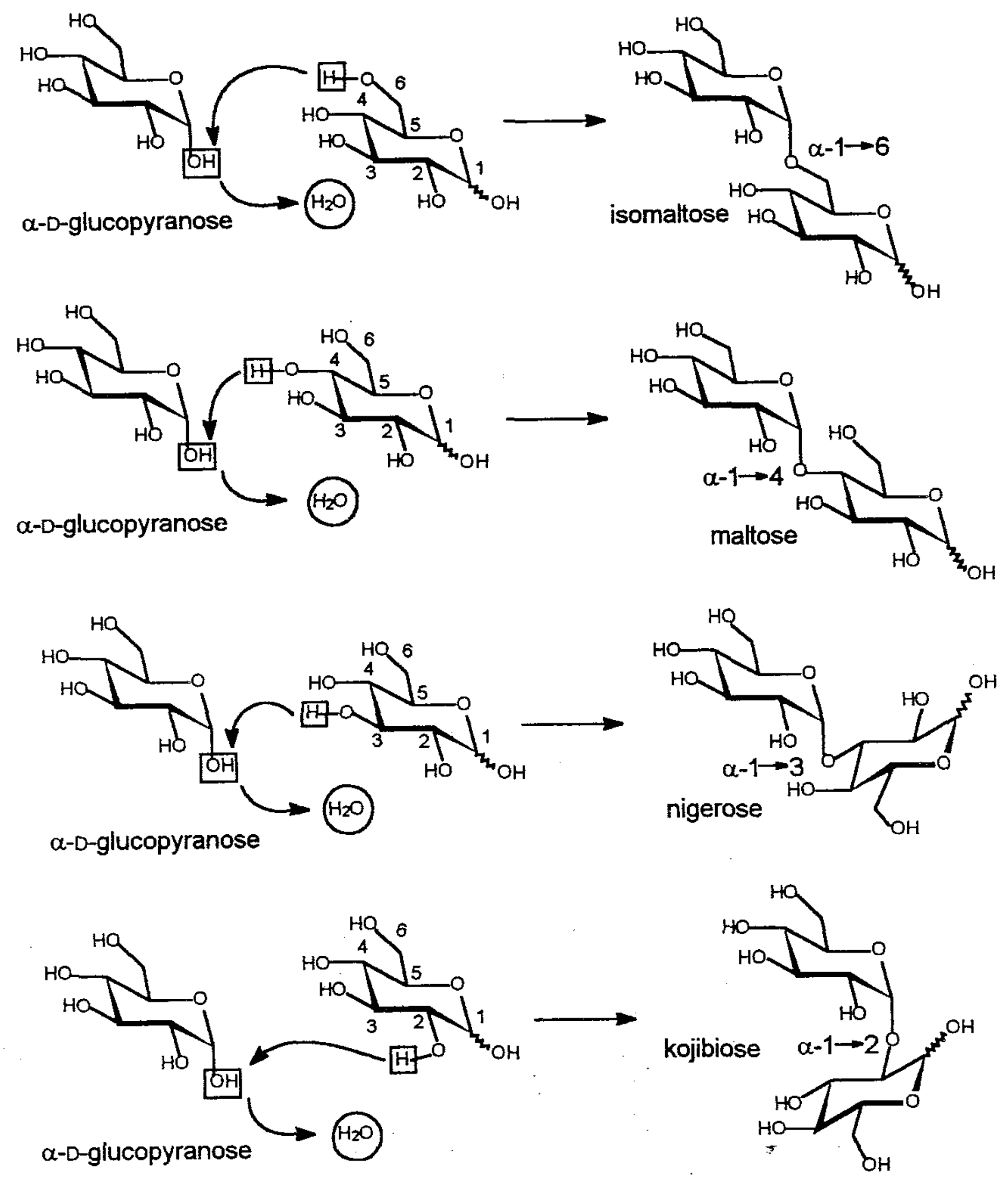
Formation of glycosidic linkages: di-, tri-, oligo- and polysaccharides

- An alcohol group can react with a hemiacetal hydroxyl group to split out water and form a glycosidic linkage
- Example: D-glucopyranose can form 11 different disaccharides, each having distinctive chemical and physical properties



Formation of the four α-linked D-glucose reducing disaccharides.

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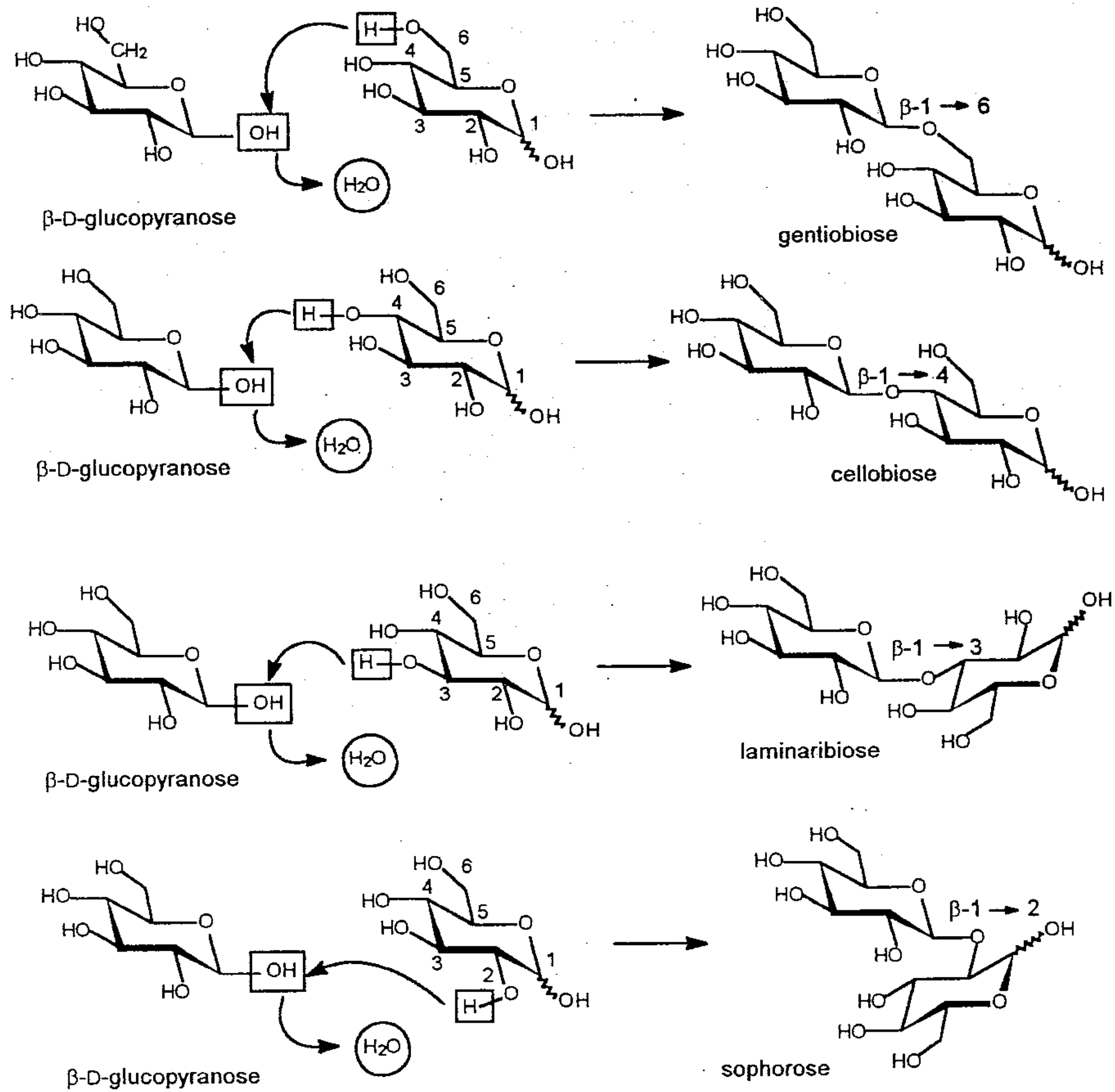

Formation of the four β-linked D-glucose-reducing disaccharides.

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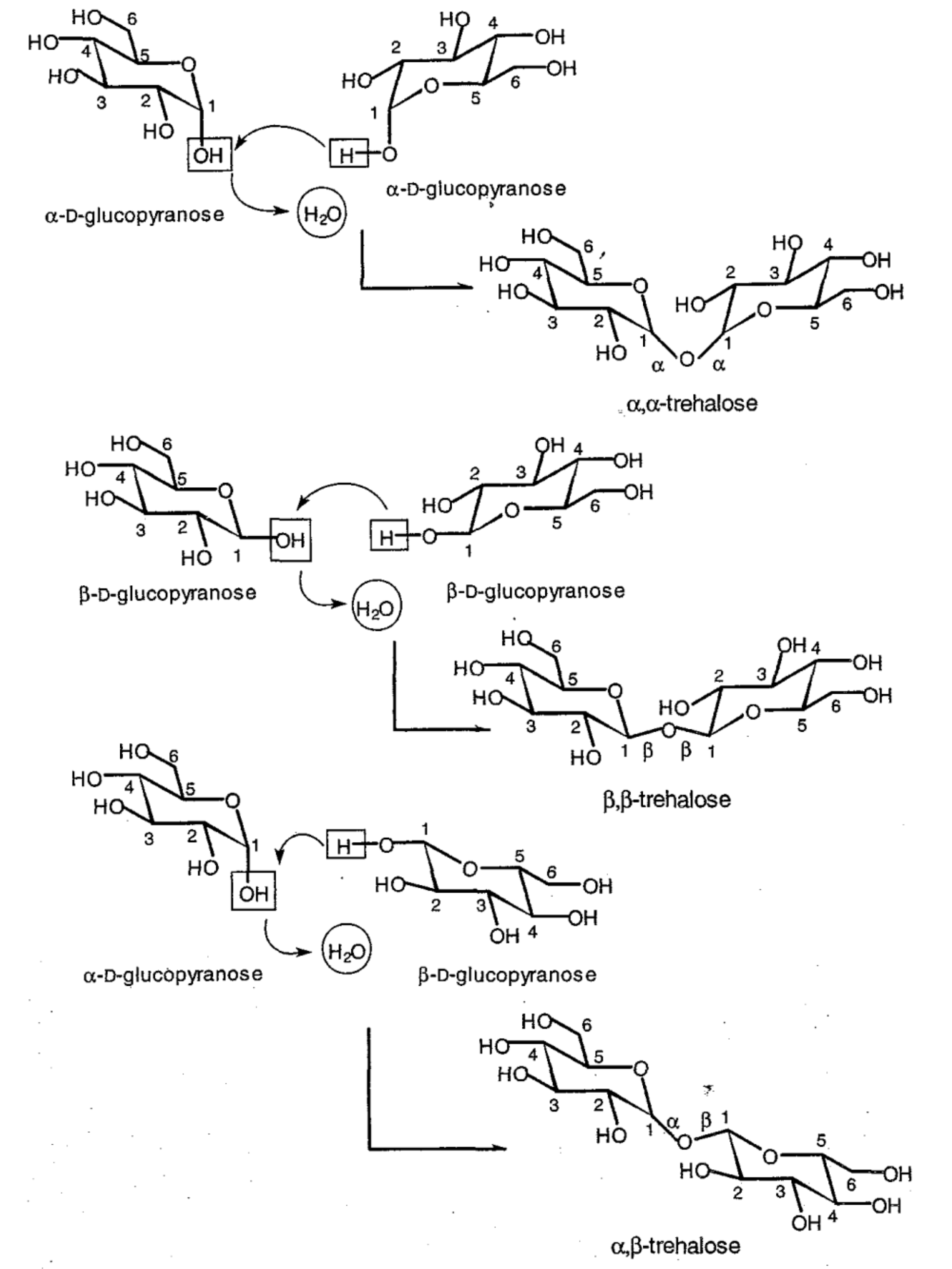
The trehaloses:
non-reducing; energy source of insects



Formation of the three possible D-glucose nonreducing disaccharides, the trehaloses.

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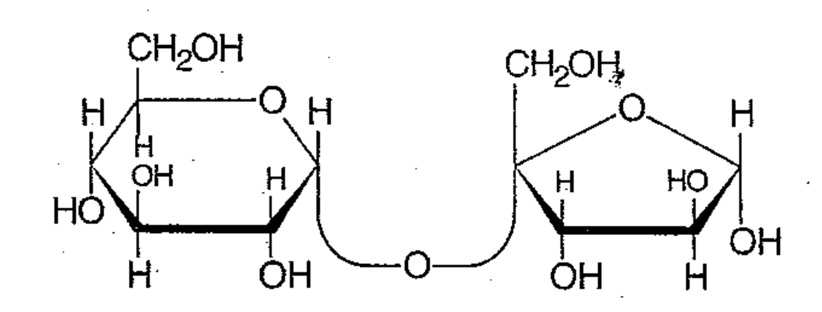
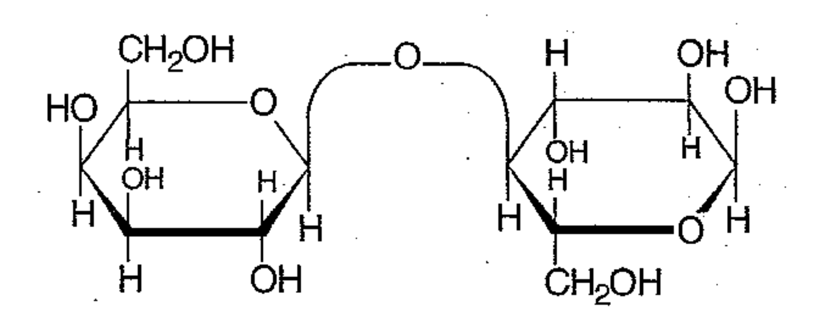
Some important di- and tri-saccharides

Sucrose



- non-reducing sugar
- α-D-glucopyranosyl-(1-2)-β-D-fructofuranose
- extracted from sugar cane and sugar beet
- sucrose is also abundantly present in most plant material, particularly in fruits
- sucrose is transported from the leaves to the other parts of the plants
- most plants convert sucrose into starch

Lactose



- reducing sugar
- β-D-galactopyranosyl-(1-4)-glucopyranose
- in milk; energy source of the new-born is produced in the mammary glands of the female
- in case of lactose intolerance: cow milk can be replaced by soya milk or coconut milk, which are devoid of lactose

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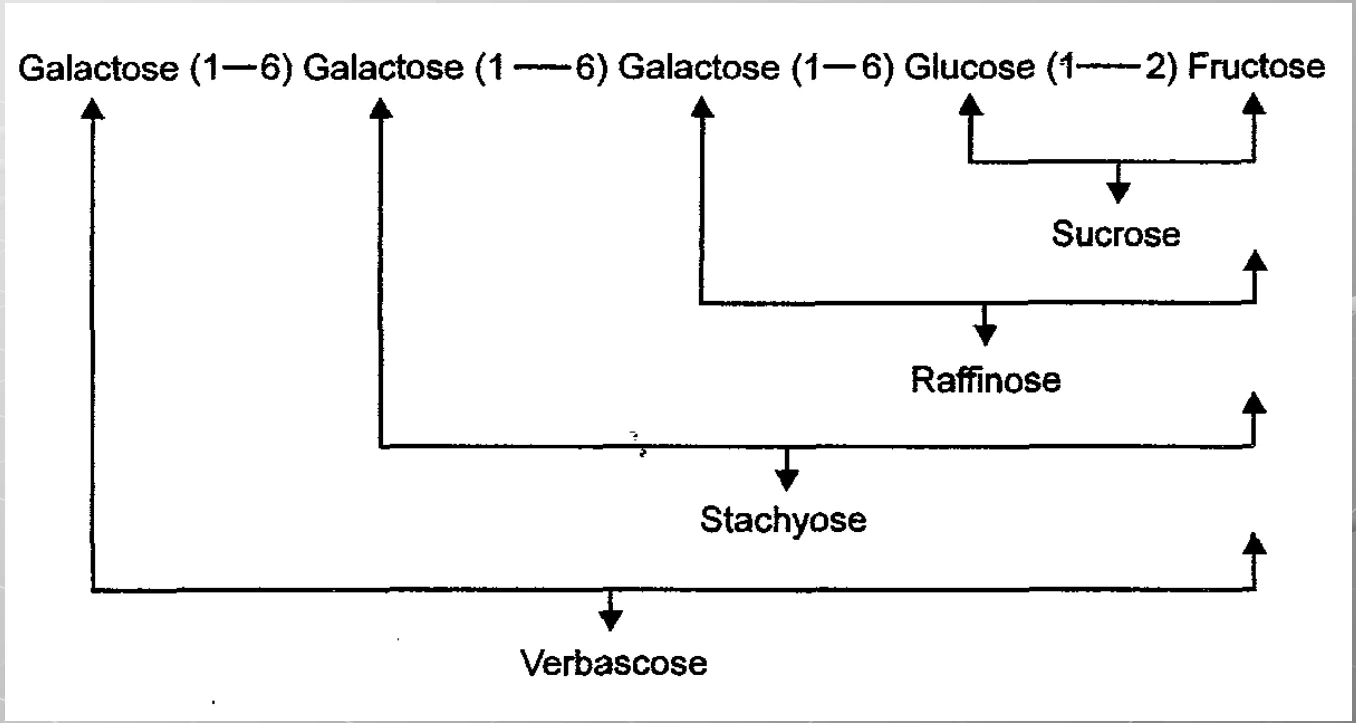
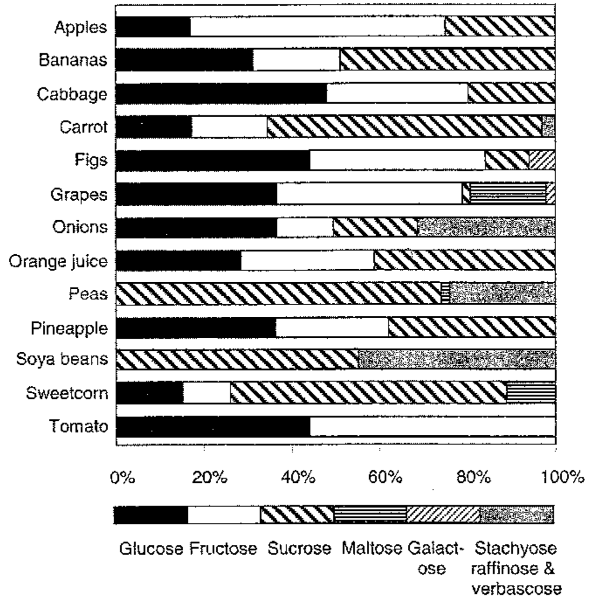
Relationship between the α-galacto-oligosaccharides sucrose, raffinose, stachyose and verbascose:



The galacto-oligosaccharides occur in many legume seeds such as soybeans, peas, beans and in some other vegetables. They are neither hydrolused, nor absorbed in the human small intestine. They are fermented in the large intestine, producing large quantities of hydrogen and carbon dioxide

flatulence

Sugar content in some foods and beverages



Representative percentage distributions of sugars in the total sugar fraction of various plant foods. There is considerable variation in these proportions depending on variety, season etc. *The contribution of sugars to the total weight of plant material also varies widely between different species.*

The total sugar contents of a variety of foods and beverages. These figures are taken from 'McCance and Widdowson' and in all cases refer to the edible portion. They should be regarded as typical values for the particular food rather than absolute figures which apply to any samples of the same food. The levels of sugars in eggs, meat, cured or fresh, poultry, game and fish, and fats such as butter and margarine are nutritionally insignificant although even traces can sometimes reveal themselves through browning at high temperatures caused by the Maillard reaction,

Food	*Total sugars (%)*	*Food*	*Total sugars (%)*
White bread	2.6	Cabbage (raw)	4.0
Corn flakes	8.2	Beetroot (raw)	7.0
Sugar coated cornflakes	41.9	Onions (raw)	5.6
Digestive biscuits	13.6	Cooking apples (raw)	8.9
Gingernuts	35.8	Eating apples (raw)	11.8
Rich fruit cake	48.4	Bananas	20.9
Cow's milk (whole)	4.8	Grapes	15.4
Human milk	7.2	Oranges	8.5
Cheese (hard)	0.1	Raisins	69.3
Cheese (processed)	0.9	Peanuts	6.2
Yoghurt (plain)	7.8	Honey	76.4
Yoghurt (fruit)	15.7	Jam	69.0
Ice cream (dairy)	22.1	Plain chocolate	59.5
Lemon sorbet	34.2	Cola	10.5
Cheesecake (frozen)	22.2	Beer (bitter)	2.3
Beef sausages	1.8	Lager	1.5
New potatoes	1.3	Red wine	0.3
Canned baked beans	5.9	White wine (medium)	3.4
Frozen peas	2.7	Port	12.0

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Polysaccharides

- Animals
  - Glycogen: energy store in liver and muscle; regulation of blood glucose level
  - Chitin: polymer of N-acetylglucosamine (exoskeletons in arthropods)
  - Proteoglycans and mucopolysaccharides: important in connective tissues
- Plants: rich source of polysaccharides. Functions:
  - Starch: energy store in tubers, seeds
  - Structural elements
- Polysaccharides important from a nutritional point of view
  - Starch: energy source (cerials: wheat, rice maize, …; potato cassava)
  - NSP (non-starch polysaccharides): cellulose, pectin, hemicellulose (fibers) are important in the healthy functioning of the large intestine; moderate the absorption of food from the small intestine.
- Polysaccharides provide texture to our food

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Polysaccharides

- Polysaccharides are linear or branched polymers with > 20 sugar units
- Scientific name: glycan – homoglycans
  – heteroglycans
- Glycosyl units are designated by the first three letters of their name, the first being capitalized;
  examples: Ara, Gal, Xyl, …
  exception: Glc = glucose
- Only L is mentioned; D is omitted
- Ring size: *p* (pyranosyl), *f* (furanosyl)
  example: αGlc*p* = α-D-glucopyranoside
- Uronic acids are designated with capital A
  example: LGul*p*A = L-gulopyranosyluronic acid
- Position of glycosidic bond: 1→3 or 1,3
- Examples
  sucrose = αGlc*p*(1→2)Fru*f*
  raffinose = αGal*p*(1→6)αGlc*p*(1→2)Fru*f*
  lactose = βGal*p*(1→4)Glc
- Note: reducing end not mentioned α or β because they occur as a mixture

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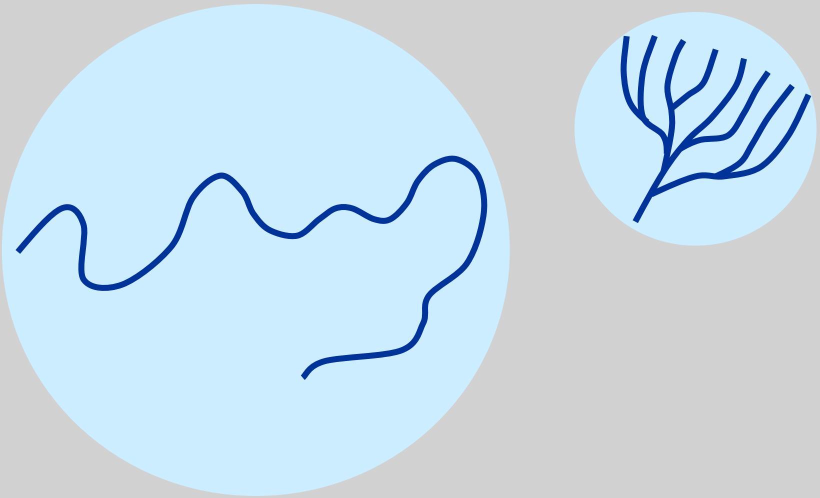
Polysaccharides: solubility

- On average, 3 –OH groups/glycosyl units ⇨ hydrogen bonding with water.
  Also ring O and glycosidic bond O form hydrogen bonds with water
  ⇨
  - high water holding capacity
  - hydrate easily
  - polysaccharides take up water, swell and usually undergo partial or complete dissolution
- Polysaccharides modify and control the mobility of water in food systems
- Polysaccharides and water control many functional properties of food, including texture
- Water hydrogen-bonded to polysaccharides does not freeze
- Polysaccharides are cryostabilizers, not cryoprotectants, i.e. they do not decrease the freezing point of water
- High- and low-molecular weight carbohydrates protect frozen food from destructive changes in texture and structure
- Water-soluble polysaccharides are called gums or hydrocolloids

Polysaccharide solution viscosity and stability

- Thickening agents; formation of gels
- The viscosity of a polymer solution is function of the size of its molecules and the conformation they adopt
- Linear polymers produce highly viscous solutions
- Viscosity depends on the DP (molecular weight), shape and flexibility of the solvated polymers
- Highly branched polysaccharides produce less viscosity than linear chains of the same molecular weight



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Polysaccharide solution viscosity and stability

- Charged polymers have an extended configuration due to repulsion of alike charges, and thus an increasing volume swept out
  ⇒ solutions of high viscosity
- Unbranched glycans that dissolve in water upon heating precipitate or gel rapidly upon cooling because of the formation of intermolecular bonds over a distance of several units
- Unbranched homoglycans have a tendency to crystallize;
  upon modification, aggregation can be prevented and stable solutions are formed (example: gums)
- Stable solutions are also formed if linear chains contain charged groups (example: Na-alginates form highly viscous solutions);
  if pH is lowered ⇒ gel formation or precipitation
- Carageenans do not precipitate because the sulfate groups remain ionized at all practical pH values

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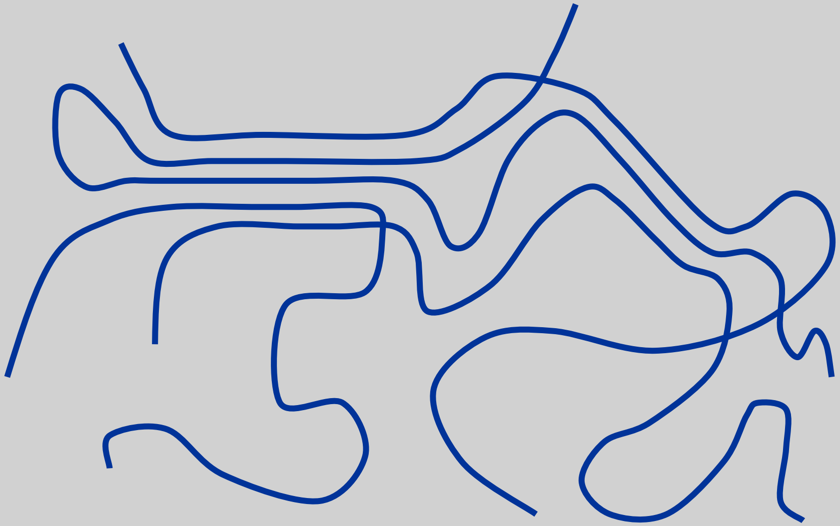
Polysaccharide gels

- A gel is a continuous 3D network of connected molecules or particles that entraps a large volume of a continuous liquid phase (cfr. a sponge)
- In gels, polymers are joined in 'junction zones' by hydrogen bonding, hydrophobic interactions, ionic interactions or covalent linkages



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Polysaccharide hydrolysis

- Glycosidic bonds are hydrolyzed by acids or enzymes
  → depolymerization
- The extent of depolymerization is determined by acid strength, time, temperature and structure of the polysaccharide
- Viscosity is reduced
- Occurs readily during thermal processing
- Enzyme-catalyzed hydrolysis depends on the specificity of the enzyme, temperature and pH

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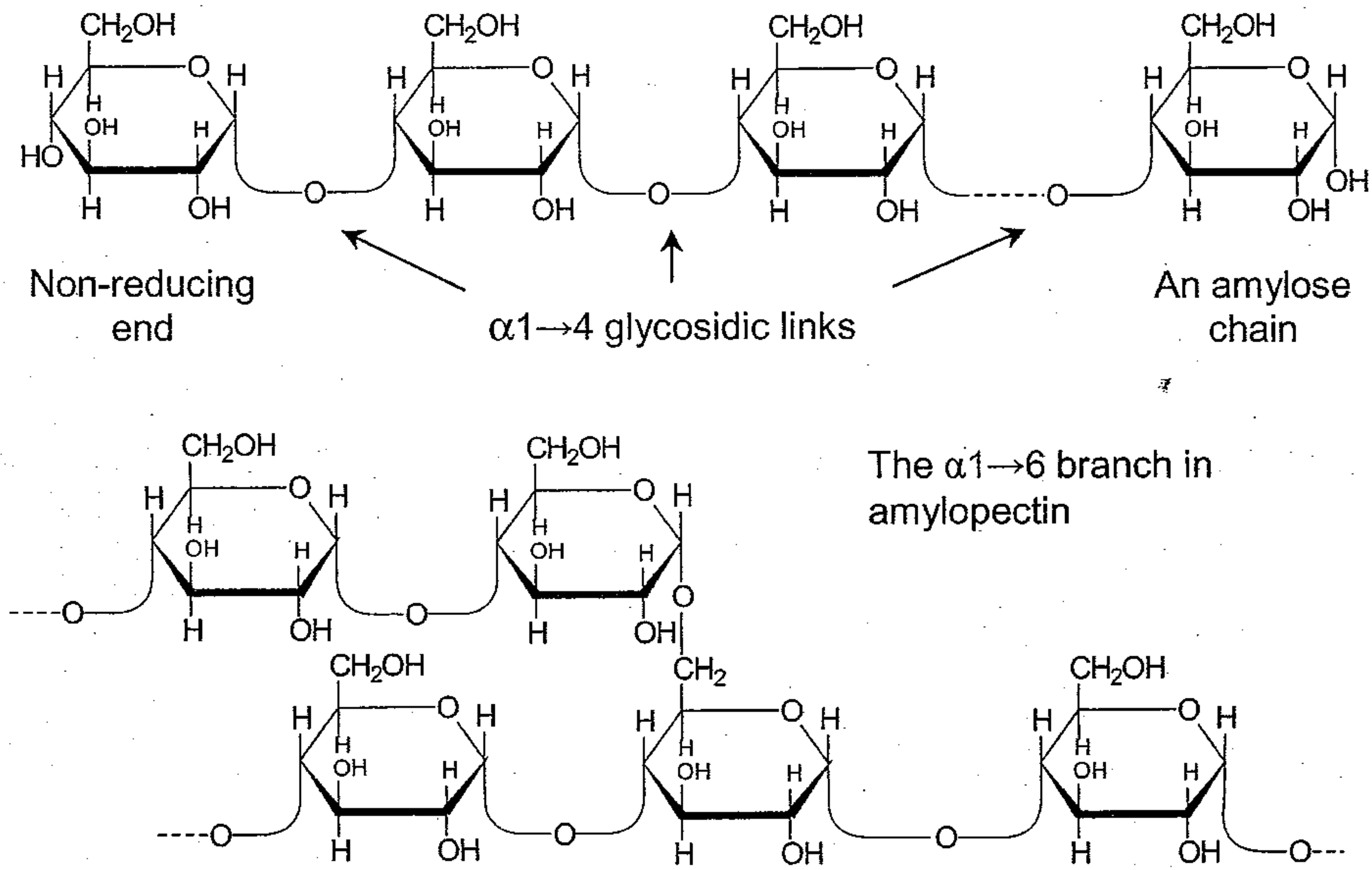
Starch

- Major food reserve of plants
- Represents 70-80% of the calories consumed by humans
- Digestible by monogastrics
- Sources: corn, waxy corn, high amylose corn, wheat, rice, tubers (potato, sweet potato, cassava), roots
- Use in food: adhesive, binding, film forming, foam strengthening, gelling, glazing, moisture retaining, stabilizing, texturizing, thickening, …
- Starch occurs as granules; insoluble and hydrates only slowly in cold water
- Viscosity-building (thickening) occurs only upon cooking
- Consists of amylose (unbranched) and amylopectin (branched) polymers

Starch content of some foods

Food	Starch (%)	Food	Starch (%)
Wheat flour (wholemeal)	61.8	Peas (petit pois)	trace
White bread	46.7	Broad beans	10.0
White rice (uncooked)	73.8	Beetroot	0.6
Spaghetti (cooked)	70.8	Broccoli	0.1
Maize (corn) flour	92.0	Carrots	0.2
Corn flakes	77.7	Chestnuts	29.6
Soya beans (raw)	4.8	Peanuts (raw)	6.3
Cassava (dry)	22.0	Walnuts	0.7
Potatoes (boiled, new)	16.7	Apples	trace
Peas (canned, processed)	14.7	Bananas	2.3

Starch



The chemical structures of amylose and amylopectin.

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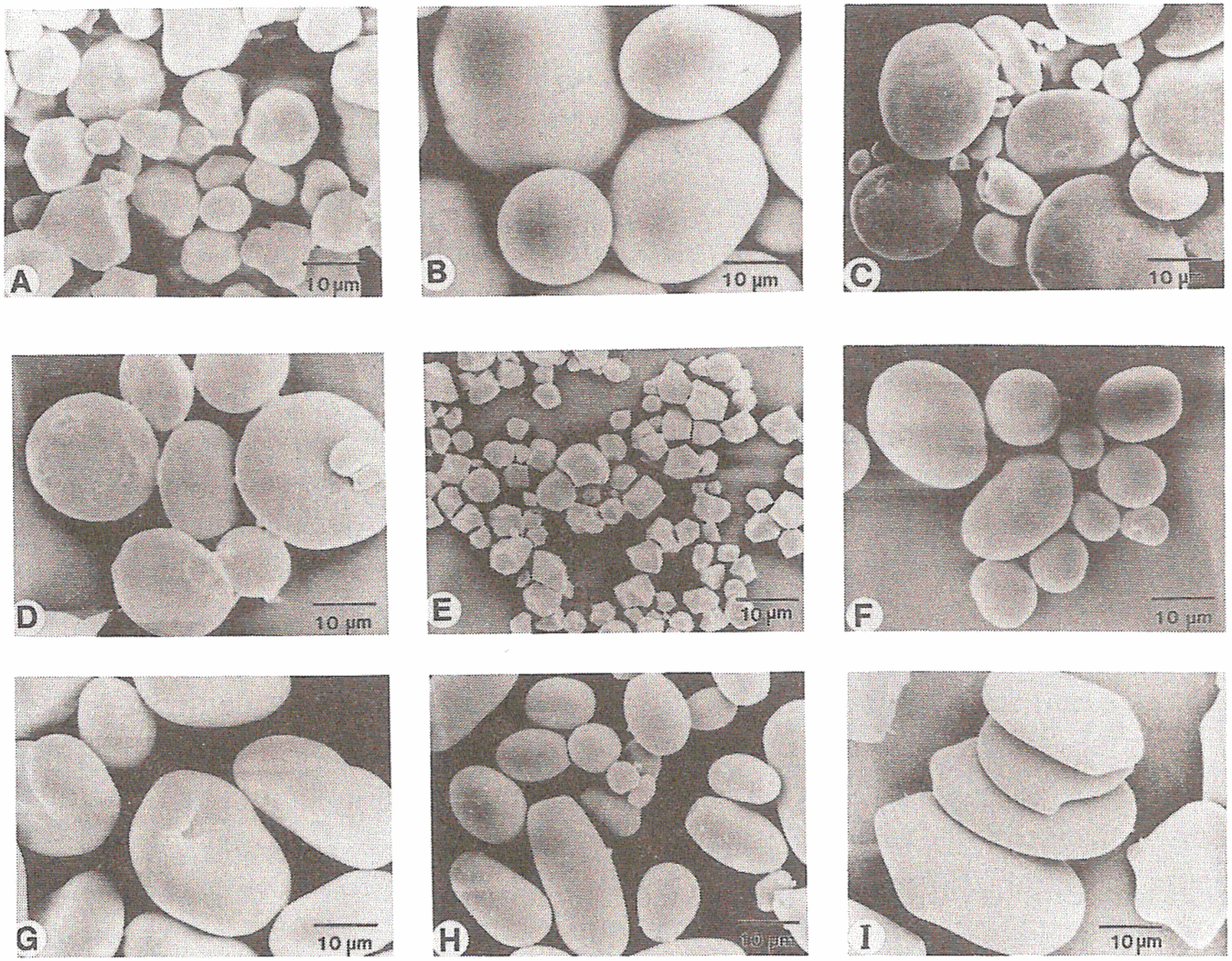
Starch



Scanning electron micrographs of starch granules: **A,** maize; **B,** potato; **C,** wheat; **D,** rye; **E,** rice; **F,** lentil bean; **G,** green pea; **H,** avocado; **I,** shoti. From ref. [2], reprinted by permission of the author and publisher.

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Starch

- Amylose:
  - Essentially non-branched (one branch in every 180-320 units, i.e. 0.3-0.5% of the linkages
  - Molecular weight of about 10^6
  - Forms right-handed helix with interior only containing H-atoms and is lipophilic; -OH groups on the exterior of the coil
  - Most starches contain about 25% amylose (high amylose corn contains 75% amylose)
- Amylopectin:
  - Highly branched molecules (4-5% of the linkages)
  - Branches occur as double helices
  - Molecular weight 10^7-$5*10^8$
  - Most common starches contain about 75% amylopectin
  - Waxy corn starch only consists of amylopectin (‘all-amylopectin’)
  - Potato amylopectin is unique in having phosphate ester groups, most often in position 6

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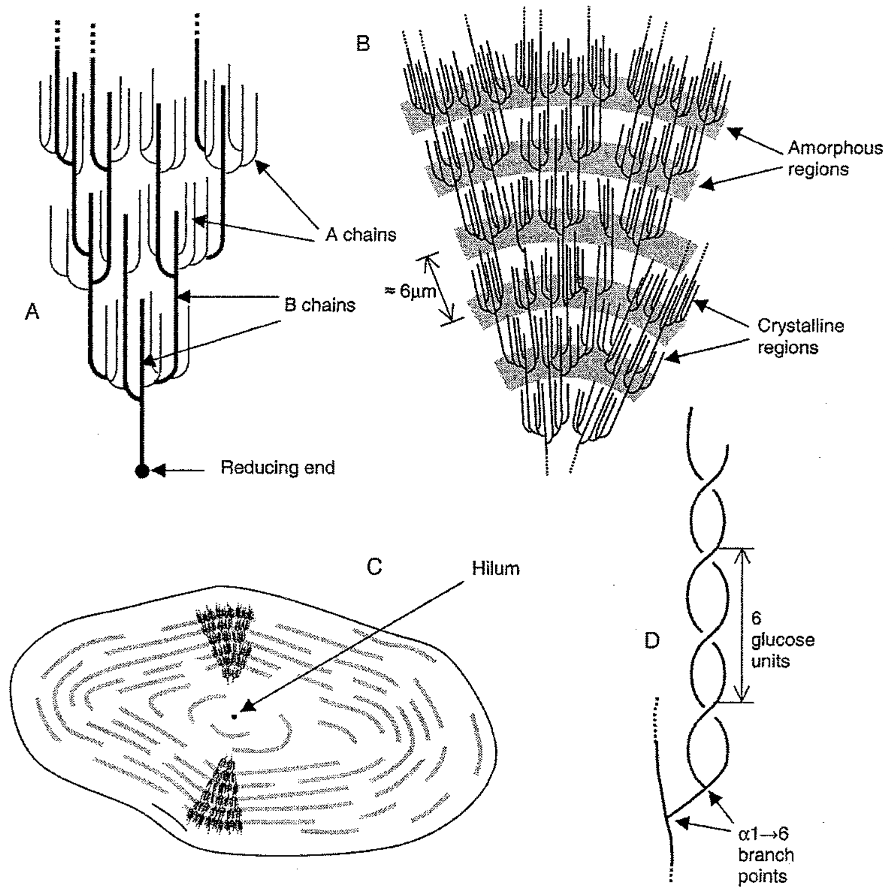
Amylopectin and the starch granule



Amylopectin and the starch granule. (A) The essential features of the cluster model first proposed by Robin in 1974. (B) The organisation of the amorphous and crystalline regions (or domains) of the structure generating the concentric layers that contribute to the 'growth rings' that are visible by light microscopy. (C) The orientation of the amylopectin molecules in a cross section of an idealised entire granule. (D) The likely double helix structure taken up by neighbouring chains and giving rise to the extensive degree of crystallinity in a granule.

Starch granules are made of amylose and amylopectin.

Branches form packed double helices ⇨ crystalline areas.

Amylose molecules occur among amylopectin molecules and some diffuse out partly in water-swollen granules.

All starches retain small amounts of ash and protein.

Potato starch contains phosphate groups that contribute to the rapid swelling in warm water and their high viscosity.

Only cereal starches contain lipids.

Starch granule composition

General Properties of Some Starch Granules and Their Pastes

	Common corn starch	Waxy maize starch	High-amylose corn starch	Potato starch	Tapioca starch	Wheat starch
Granule size (major axis, μm)	2–30	2–30	2–24	5–100	4–35	2–55
Amylose (%)	28	< 2	50–70	21	17	28
Gelatinization/pasting temperature (°C)[a]	62–80	63–72	66–170[b]	58–65	52–65	52–85
Relative viscosity	Medium	Medium high	Very low[b]	Very high	High	Low
Paste rheology[c]	Short	Long (cohesive)	Short	Very long	Long (cohesive)	Short
Paste clarity	Opaque	Very slightly cloudy	Opaque	Clear	Clear	Opaque
Tendency to gel/retrograde	High	Very low	Very high	Medium to low	Medium	High
Lipid (%DS)	0.8	0.2	—	0.1	0.1	0.9
Protein (%DS)	0.35	0.25	0.5	0.1	0.1	0.4
Phosphorus (%DS)	0.00	0.00	0.00	0.08	0.00	0.00
Flavor	Cereal (slight)	"Clean"		Slight	Bland	Cereal (slight)

[a]From the initial temperature of gelatinization to complete pasting.
[b]Under ordinary cooking conditions, where the slurry is heated to 95–100°C, high-amylose corn starch produces essentially no viscosity. Pasting does not occur until the temperature reaches 160–170°C (320–340°F).
[c]For a description of long and short flow, see Section 4.3.2.

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Starch granule gelatinization and pasting

- Undamaged starch granules are insoluble in cold water, but can imbibe water reversibly
- In heated water granules undergo gelatinization
- Gelatinization is a disruption of the ordered structure within the granule → swelling, loss of birefringence, loss of crystanility, leaching of amylose
- Gelatinization occurs within a certain temperature range
- Upon continued heating → total disruption of the granules and formation of a starch paste (viscous mass)
- Starch paste consists of solubilized amylose and amylopectin molecules and granule remnants or ghosts, i.e. the outer portion of the granule which is insoluble
- Cooling of a hot paste results in a visco-elastic rigid gel

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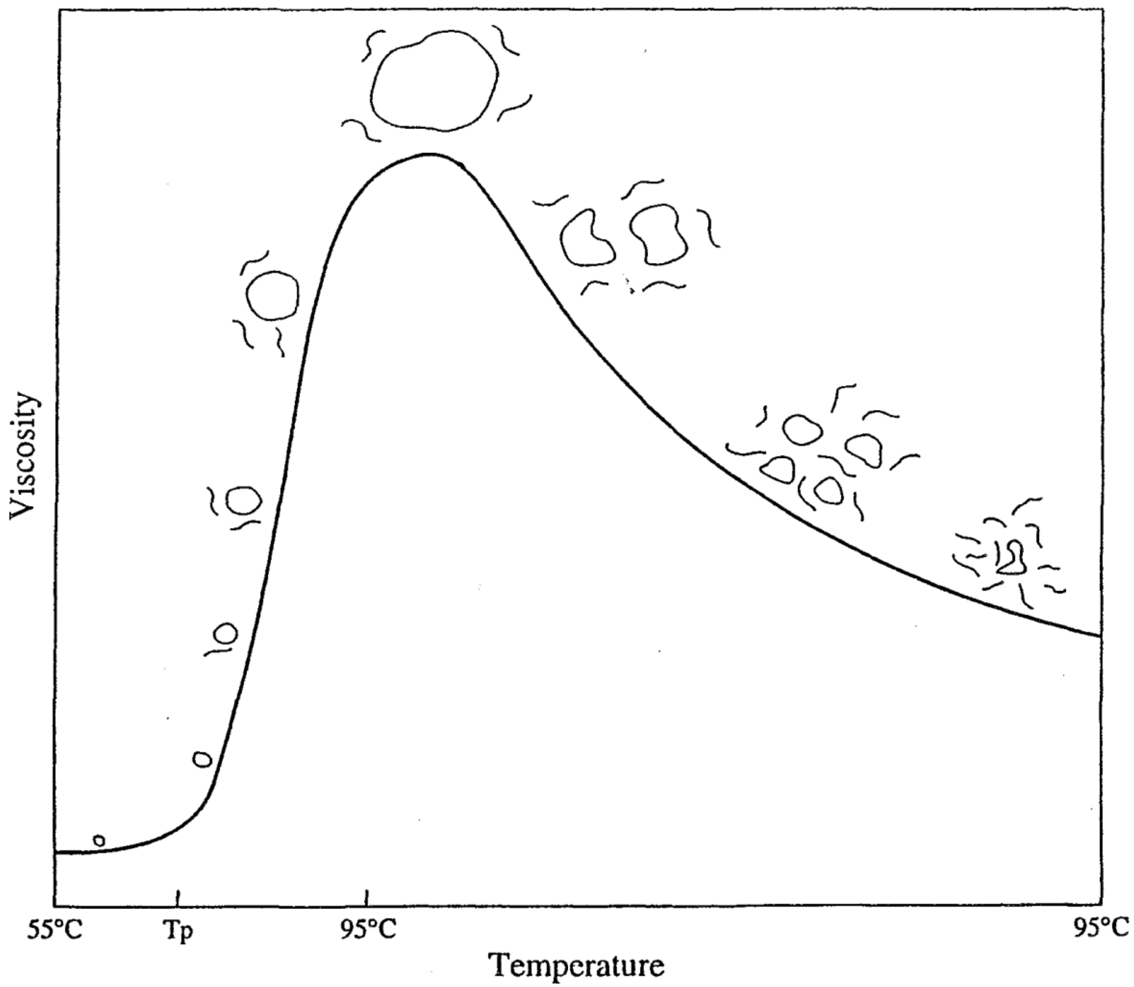
Starch granule gelatinization and pasting



Representative Brabender Visco/amylo/graph curve showing viscosity changes related to typical starch granule swelling and disintegration as a granule suspension is heated to 95°C and then held at that temperature. (The instrument imparts moderate shear to the system.) Tp is the pasting temperature, that is, the temperature at which a viscosity increase is recorded by the instrument.

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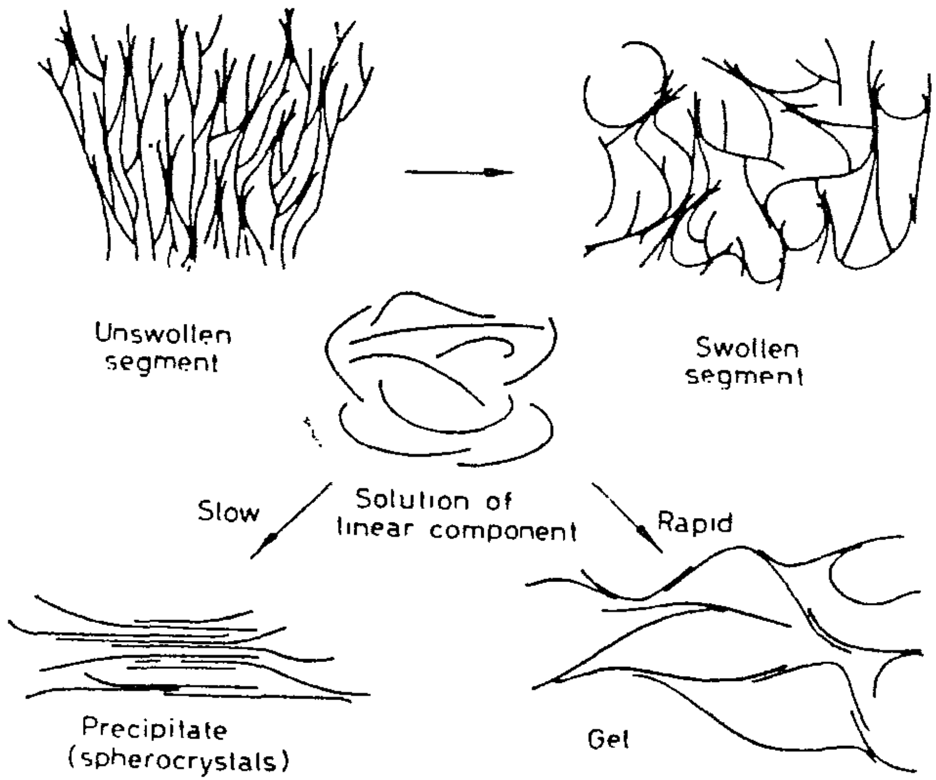
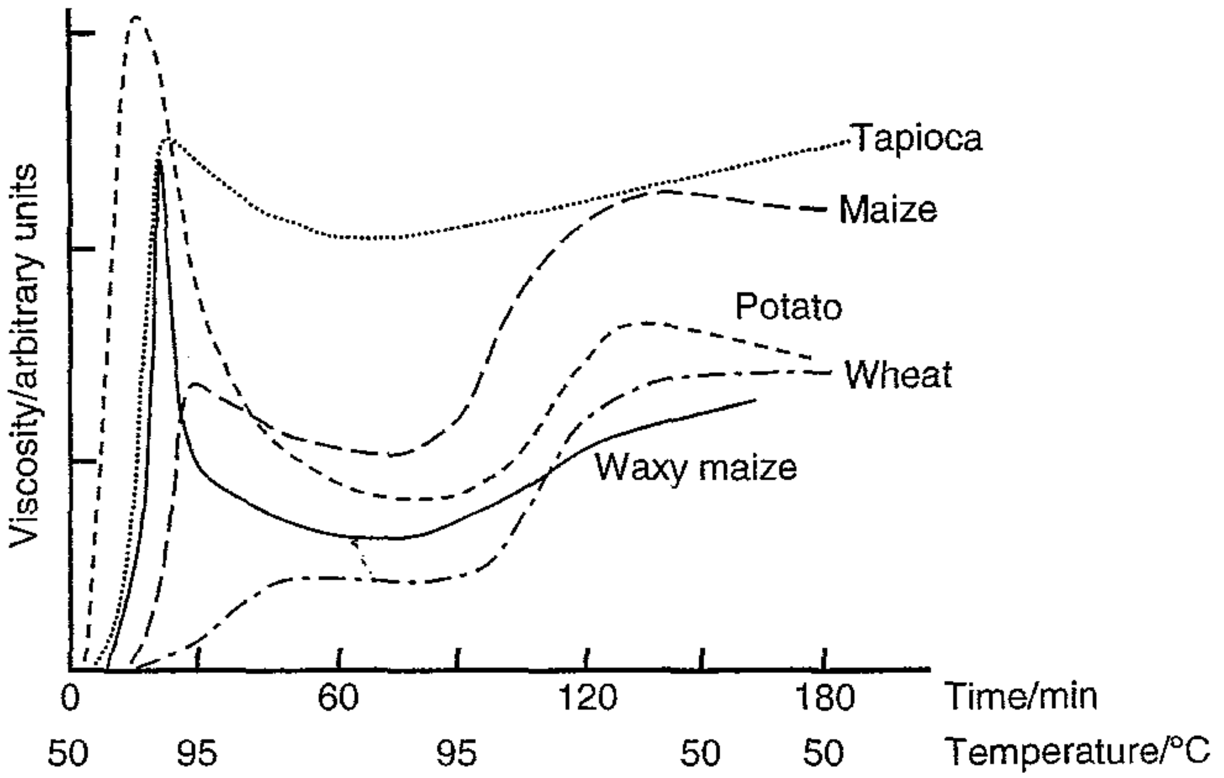
Starch granule gelatinization and pasting



Schematic Representation of the Behavior of Starch on Swelling, Dissolving, and Retrograding. *Source:* From J.A. Radley, Technical Properties of Starch as a Function of Its Structural Chemistry, in *Recent Advances in Food Science,* Vol. 3, J.M. Leitch and D.N. Rhodes, eds., 1963, Butterworth.

Starch granule gelatinization and pasting



Brabender Amylograph traces of the gelatinisation of a number starches. The temperature is raised steadily from 50 to 95 °C over the first half hour period. It is then maintained at 95 °C for one hour and then brought down back to 50 °C over the final half hour period.

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Starch complexes

- Amylose chains are helical with hydrophobic (lipophilic) interiors that can form complexes with hydrophobic portions of other molecules that fit within the hydrophobic interior
- Iodine (as I_3^-) complexes are formed with amylose and amylopectin
  ⇨ blue colour with amylose
  reddish-purple colour with amylopectin
- Polar lipids can form complexes that affect gelatinization, the rheological properties and crystallization of starch molecules

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Starch hydrolysis

- Acid hydrolysis
  - Depolymerization by hot acids: fragmentation with HCl
    ⇨ initially large fragments are formed
  - Products are still granular but break up easily; these starches are called ‘acid-modified’ or ‘thin-boiling’ starches
  - Acid modified starches form gels with improved clarity & increased strength
  - Upon extended acid modification, dextrins are formed
  - Continued hydrolysis
    ⇨ D-glucose, maltose & other malto-oligosaccharides
    ⇨ stable syrups that do not crystallize easily
- Enzymatic hydrolysis
  - α-amylase: endo-enzyme that cleaves both amylose and amylopectin
    ⇨ oligosaccharides; acts only on $\alpha 1 \rightarrow 4$ linkages
  - Glucoamylase: exo-enzyme, cleaves both $\alpha 1 \rightarrow 4$ and $\alpha 1 \rightarrow 6$ linkages
    ⇨ D-glucose
  - β-amylase: releases maltose units from the reducing end of amylose; also attacks amylopectin but does not cleave $\alpha 1 \rightarrow 6$ bonds
    ⇨ ‘limit dextrin’
  - Isoamylase: debranching enzyme
    ⇨ linear low molecular weight oligosaccharides

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Modified food starch

- Depolymerization:
  starch granules treated with HCl followed by neutralization
  ⇨ limited number of glycosidic bonds are cleaved
  ⇨ more easily gelatinization
- Derivatization:
  esterification of <1% of the glucose units with e.g. organic acids gives 'stabilized starches'
  ⇨ gels with excellent freeze-stability, high paste viscosity or emulsifying capacity
- Cross-linking:
  strengthen the granule structure
  ⇨ slow gelatinization
  Applied in canned products: heating is possible and heat transfer is not impaired by solidification

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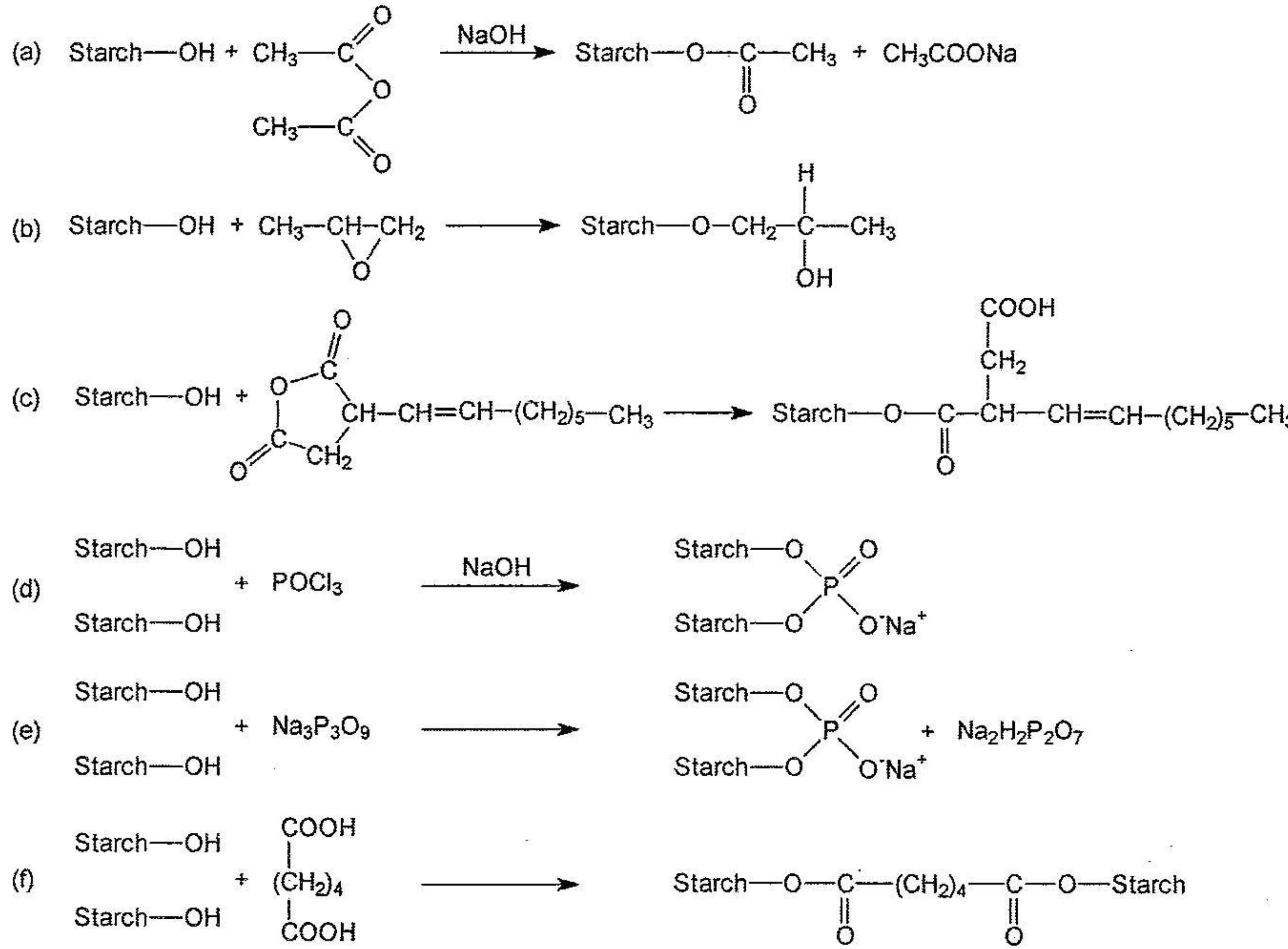

Chemical modification of starch. Reactions (a)–(c) *are stabilising derivitisations,* (d)–(f) *are crosslinking reactions.* (a) *Acetylation with acetic anhydride.* (b) *Formation of a hydroxypropyl ether by reaction with propylene oxide.* (c) *Formation of the 2-(octenyl-1)succinyl ester.* (d) *Phosphate diester formation with phosphorus oxychloride.* (e) *Phosphate diester formation with sodium trimetaphosphate.* (f) *Adipate diester formation with adipic acid.*

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Cellulose, hemicellulose and fiber

- Cellulose and hemicellulose are major components of plant foods known as ‘dietary fiber’
- Other types of fiber: gums, seaweed, polysaccharides, pectins, resistant starch and inulin
- Common characteristics:
  - They are not broken down in the small intestine of monogastrics, but to some degrees these polymers are by resident bacteria of the large intestine ⇨ production of H_2, CO_2, methane, short-chain fatty acids (acetic acid, propionic acid, butyric acid, lactic acid); some of these end products are reabsorbed by the lining of the colon and used as energy source
- Definition of dietary fiber according to the ‘American Association of Cereal Chemists’:

  Dietary fiber is the edible parts of plants or analogous carbohydrates that are resistant to digestion and absorption in the human small intestine with complete or partial fermentation in the large intestine. Dietary fiber includes polysaccharides, oligosaccharides, lignin and associated plant substances. Dietary fibers promote beneficial physiological effects including laxation, and/or blood cholesterol attenuation and/or blood glucose attenuation.

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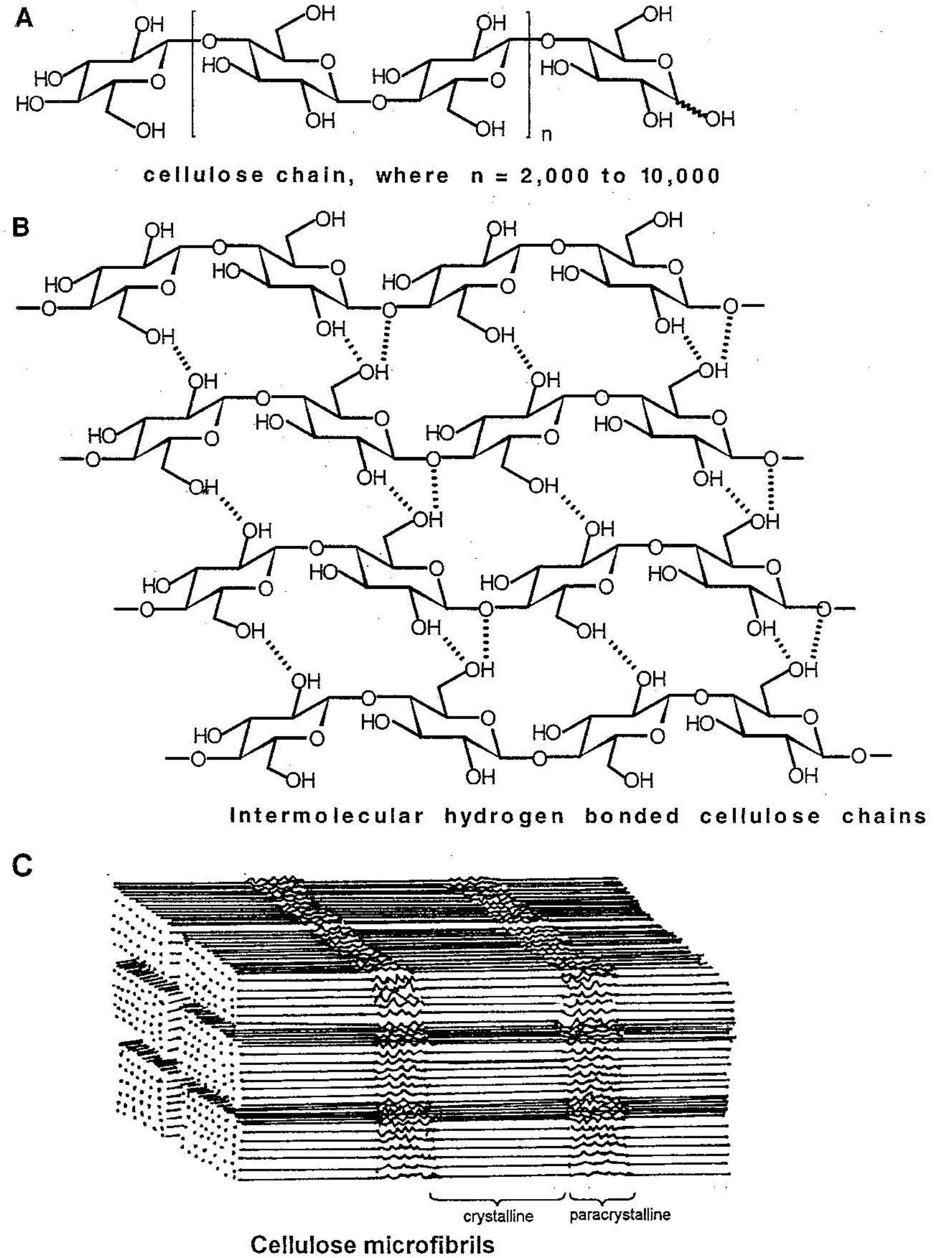
Cellulose: structure

- Cellulose: the most abundant organic chemical on earth; essential component of all cell walls
- Cellulose consists of at least 3,000 $\beta 1 \rightarrow 4$ linked glucopyranose units
- Cellulose molecules pack into microfibrils of several µm in length and of 3-10 nm diameter
- Stabilization through inter-chain hydrogen bonding ⇨ insoluble



Structure of cellulose: **A,** Structural formula for cellulose; **B,** intermolecular hydrogen bonded cellulose chains; **C,** structure of cellulose microfibrils,

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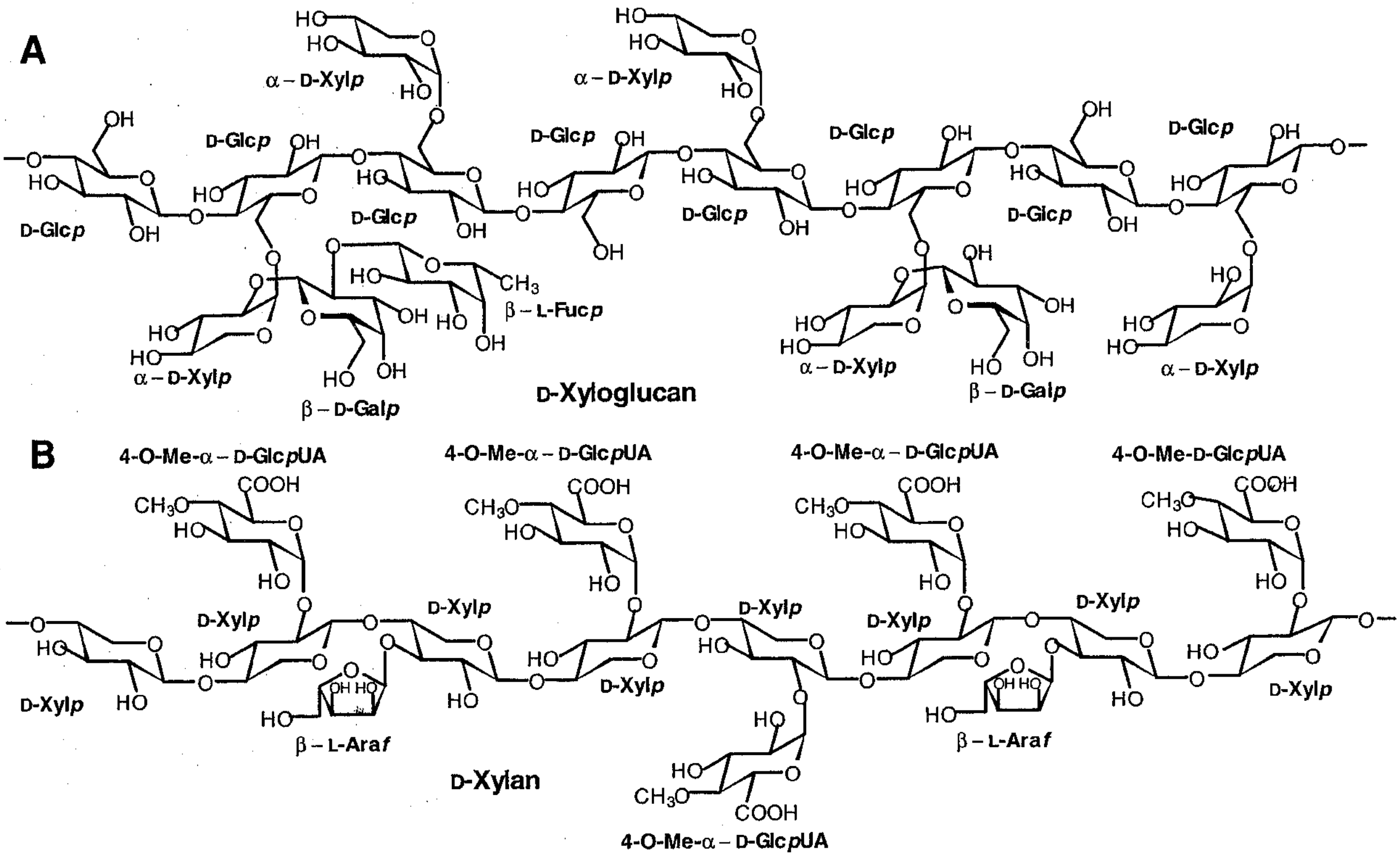
Cellulose, hemicellulose and fiber

- Ruminants digest cellulose thanks to bacteria in their rumen that secrete cellulotic enzymes ⇨ glucose that is fermented to short-chain fatty acids (example: butyric acid that is used by the animal as energy source)

- ## Hemicellulose:

  associated with cellulose from which it can be released by alkaline solutions (e.g. 15% KOH)
- Three types of hemicellulose:
  - Xylans
  - Mannans and glucomannans
  - Galactans and arabinogalactans

Hemicellulose: some examples



Structures of the major hemicelluloses: **A,** D-xyloglucan; **B,** D-xylan.

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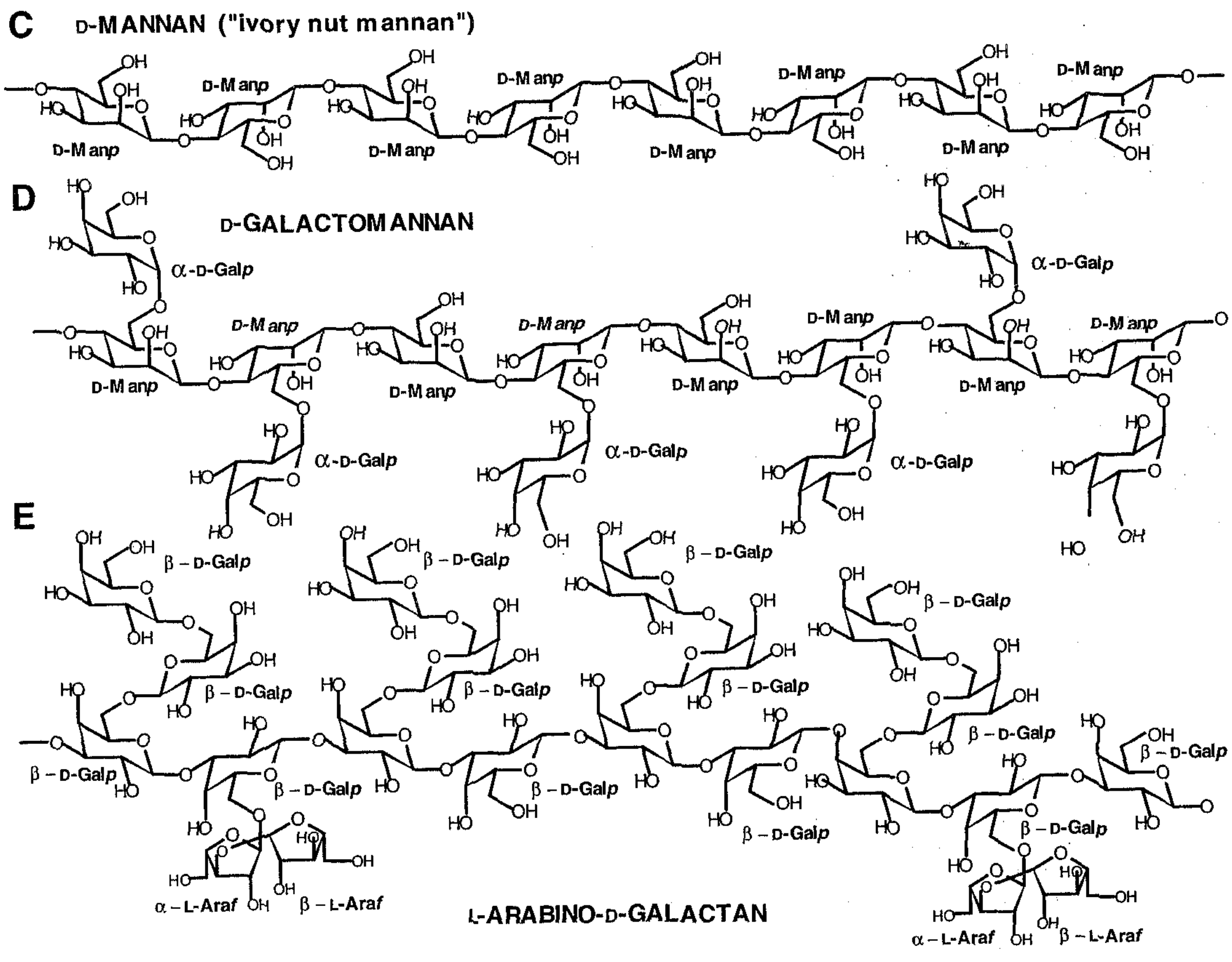
Hemicellulose: some examples



C, D-mannan; D, D-galactan; E, L-arabino-D-galactan.

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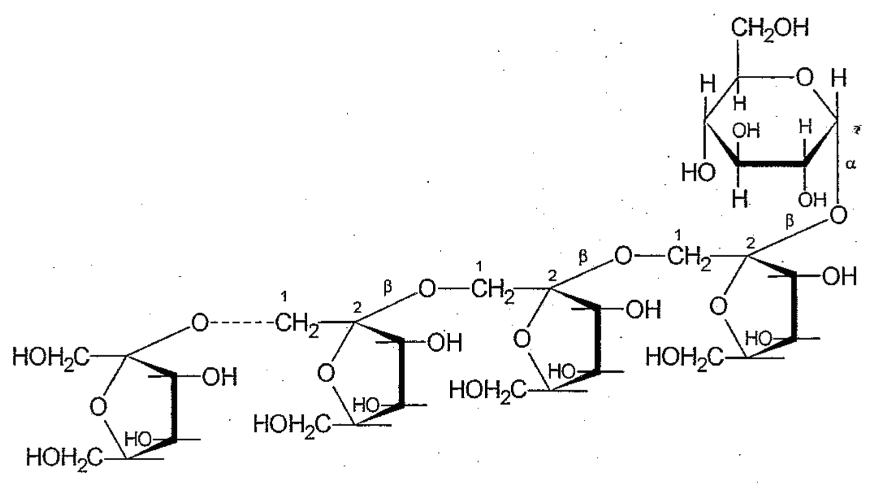
Cellulose, hemicellulose and fiber

- Xylans of cereals are best known and are a dominant group
  - Linear or occasionally branched β1→4 linked xylopyranose with single arabinose and glucuronic acid
    ⇨ because of branching no tight packing as in cellulose
- Xylans are major components of cereal grains

- β-Glucans: those of oat are best known
  - Every 3 or 4 glucose units, there is a β1→3 instead of a β1→4 linkage
  - They form highly viscous solutions
  - Are supposed to have a beneficial effect on blood cholesterol level by interfering with cholesterol and bile salt uptake in the small intestine

Cellulose, hemicellulose and fiber

- Inulin:
  - Is a polymer of fructose
  - Is present in huge quatities in the roots of chicory (*Cichorium intybus*) and Jerusalem artichokes (*Helianthus tuberosus*); the roots of both plants contain around 18 g inulin per 100 g fresh weight; small amounts are also present in asparagus, onion, garlic, bananas and cereal flours
  - Inulin resists digestion in the human stomach and small intestine, but is fermented in the colon, yielding considerable amounts of short chain fatty acids such as acetic propionic and butyric acids and promotes the growth of bifidobacteria



The β-(2→1) linked fructofuranose chain of inulin. A sucrose residue is usually found providing a non-reducing terminus for what would otherwise be the reducing end of the chain.

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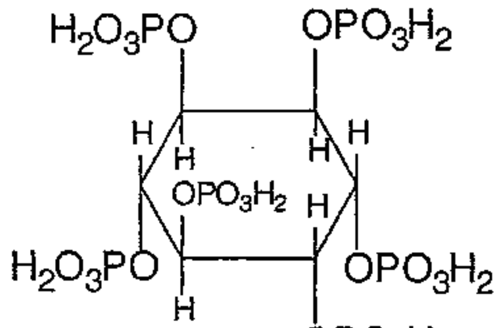
Cellulose, hemicellulose and fiber

- Presumed nutritional benefits of high fiber diets:
  - Lower incidence of bowl disorders (constipation & cancer)
  - Reduction of the residence time of potential carcinogens derived from other food components
  - Short-chain fatty acids such as acetic acid, propionic acid and butyric acid induce apoptosis of bowl tumor cells
- Although dietary fibers are generally considered to be important and health-promoting components of the diet, the association of phytic acid (inositol hexaphosphate) is an important component of bran
- Phytic acid is a phosphate reserve of germinating seeds and the phosphate groups can complex divalent cations such as Ca^{2+} and Zn^{2+}



Phytic acid

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Cellulose, hemicellulose and fiber

- Pectins
  - Major component of the middle lamella of plant tissues
  - Important proportion of the structural material of soft plant tissues such as parenchyma of soft fruit and freshy roots
  - Polymers of galacturonic acid linked $\beta 1 \rightarrow 4$
  - A proportion of the COOH groups are methylated (60% in apple pulp and citrus peel, 10% in pectin from strawberries)
  - Up to 20% of the sugars in pectin consist of L-rhamnose, D-glucose, D-galactose, L-arabinose and D-xylose
  - L-rhamnose is present in all pectins and cause kinks in the structure
  - Apple pectin is best known:
    it is an extended rhamnogalacturonan that contains regions that are free of rhamnose, i.e. smooth regions
    smooth regions are interspersed by ‘hairy’ regions consisting of short branches of arabinogalactans (citrus peel) or of xylose (apple pectin)
  - Pectins form a gel that is the basis of jams
  - Pectin gels consist mainly of water and yet are stable
  - Gels are stabilized by junction zones, i.e. regions of ordered structure that are crystalline in nature

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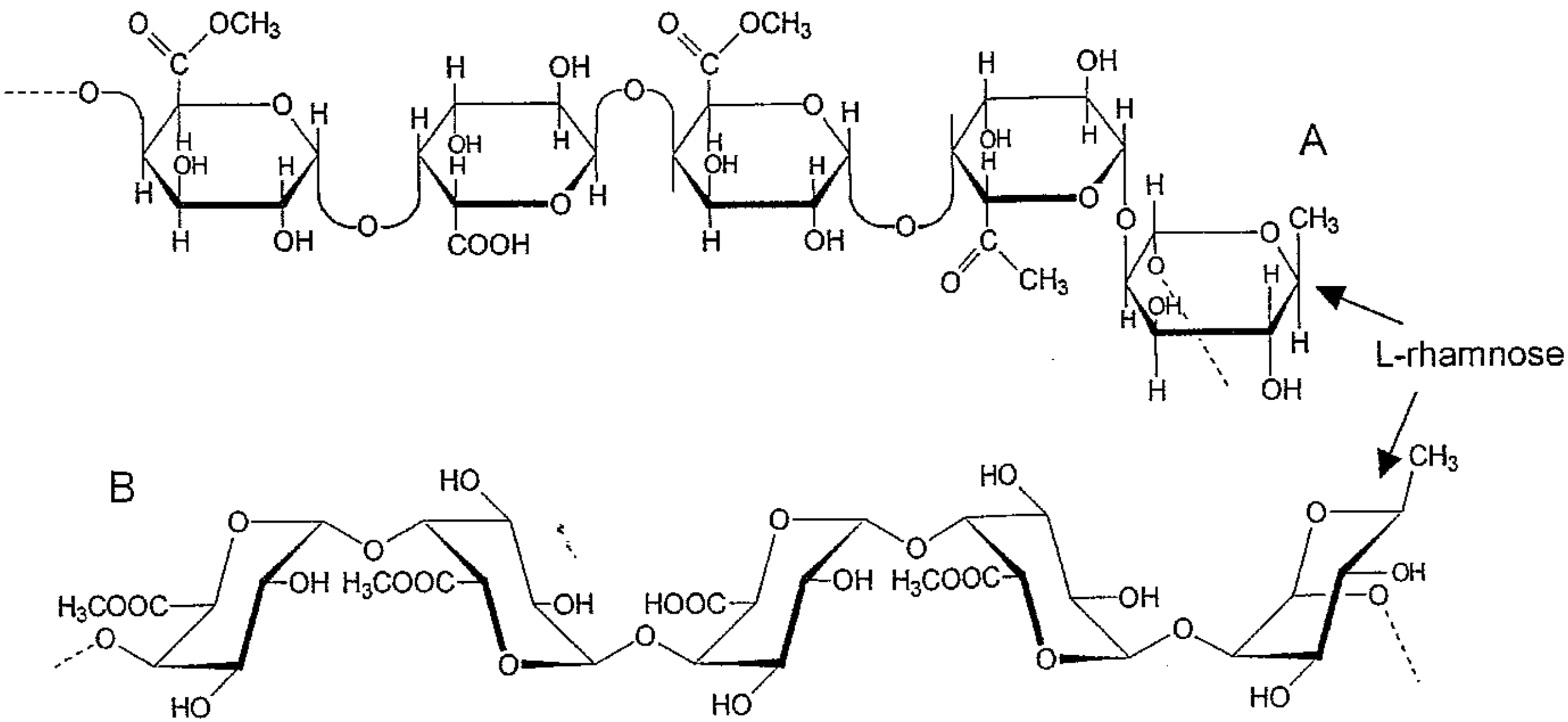
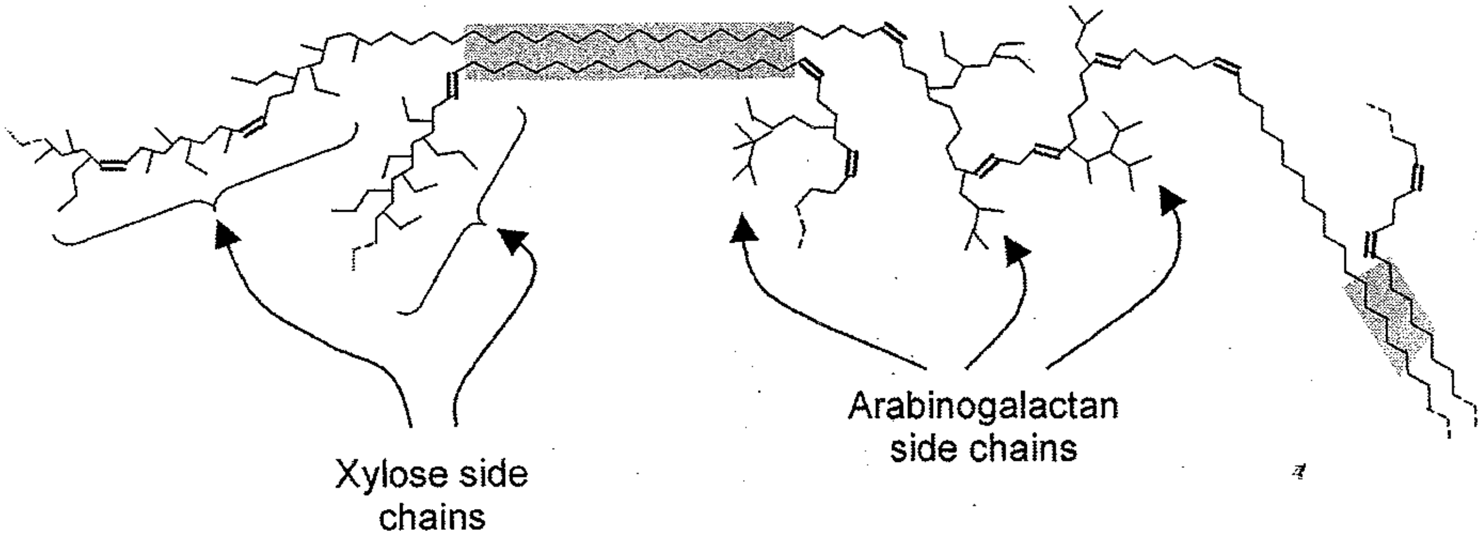
Cellulose, hemicellulose and fiber



The polygalacturonan backbone of pectin. (A) shows four galacturonic acid residues, three of which are methylated, and a rhamnose residue. (B) shows the same structure in their chair configuration to illustrate the zig-zag shape of the chain. Ring hydrogen atoms have been omitted for clarity. The effect of the rhamnose residue on the configuration of the chain is clear.

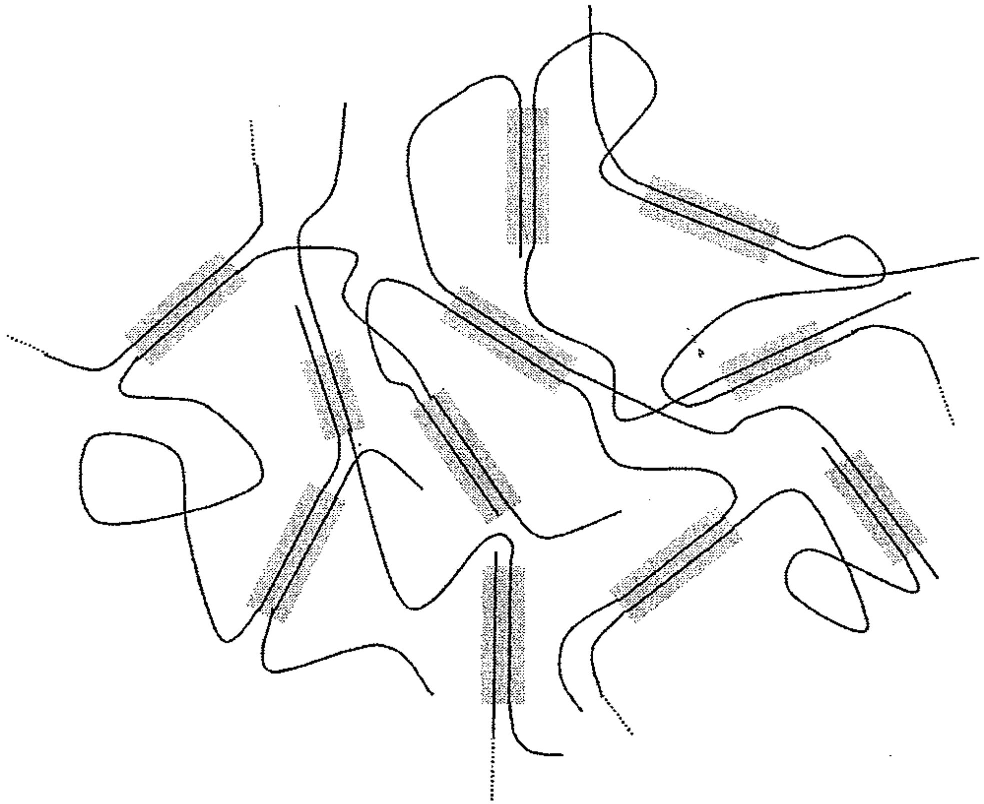
Cellulose, hemicellulose and fiber



A suggested arrangement for the rhamnogalacturonan backbone and neutral sugar side chains based on Pilnik's studies of apple pectin. Each line in the zig-zag of the backbone represents a galacturonate unit, with or without an esterified methyl group, except where a double line indicates the presence of a rhamnose residue. Junction zones formed from paired 'smooth' regions of the backbone are shaded.

* Terms such as galacturonan, glucan and arabinogalactan describe polysaccharides consisting of, respectively, galacturonic acid, glucose and both arabinose and galactose. The 'an' suffix is derived from 'anhydro', indicating that the links between the monosaccharide units are formed by the departure of the elements of water.

Cellulose, hemicellulose and fiber



A generalised, two-dimensional view of a polysaccharide gel. Regions of the polymer chains involved in junction zones are shaded. Between them the polymer chains form regions of irregular orientation, so-called random coils. Water, dissolved substances and suspended particles occupy the spaces between the chains. Each end of the junction is terminated by an anomalous residue or the presence of a bulky side chain on at least one of the chains involved. The junction zones of some polysaccharides may involve many chains stacked together, rather than the pairs shown here.

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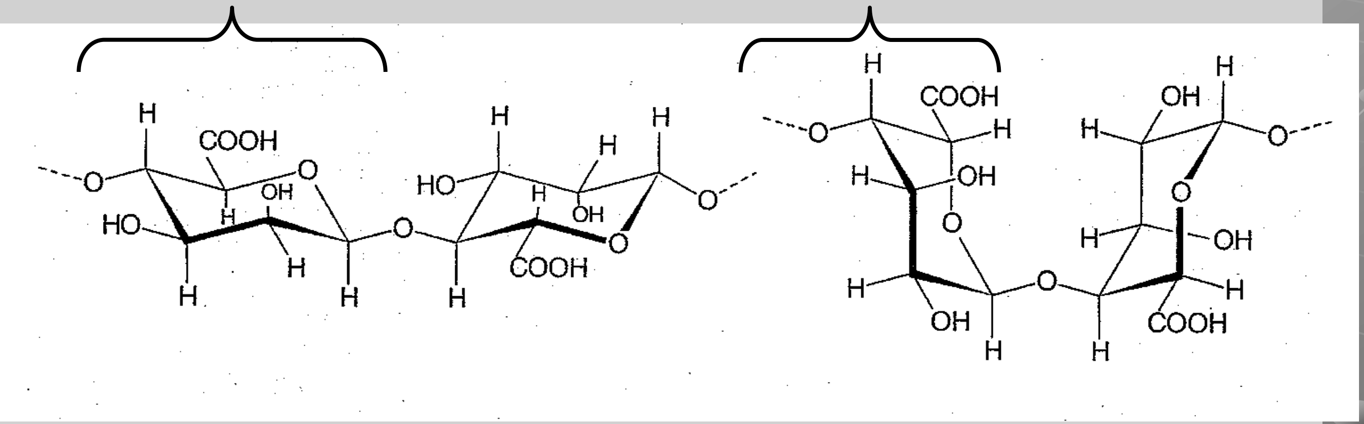
Cellulose, hemicellulose and fiber

- Pectin breakdown during fruit ripening by pectinases
  - Pectin methyl esterase removes methanol residues
  - Polygalacturonases hydrolyze the glycosidic bonds between demethylated galacturonic acid residues; there are two types, i.e. exo- and endo-polygalacturonases
  - Pectin lyases break glycosidic bonds between methylated galacturonic acid residues
- Pectinases are also produced by bacteria and fungi that cause rotting of fruits and vegetables

Cellulose, hemicellulose and fiber

- Seaweed polysaccharides
  - Alginates: produced by brown algae, i.e. *Pheophyceae*
  - Agars and carageenans: produced by red algae, i.e. *Rhodophyceae*
- <u>Alginates</u>: linear polymers of two different monosaccharide units, i.e. β-D-mannuronic acid (M) and α-L-guluronic acid (G)

M & G are C5 epimers of each other



  - M block regions are flat ribbon-like, similar to the conformation of cellulose because of the equatorial bonding
  - G block regions have a pleated conformation as a result of its axial-axial glycosidic bonds
  - M and G occur in three different sequences:

-M-M-M-M-M- **-G-G-G-G-G-** **-M-G-M-G-M-G-**

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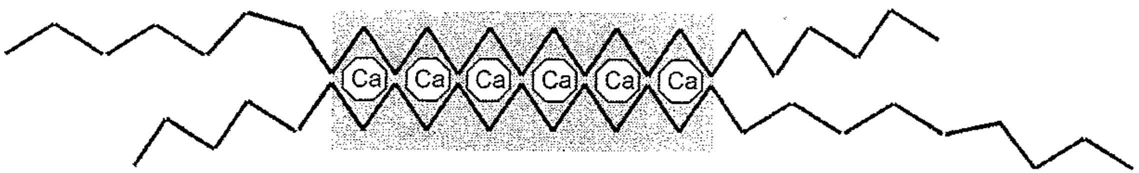
Cellulose, hemicellulose and fiber

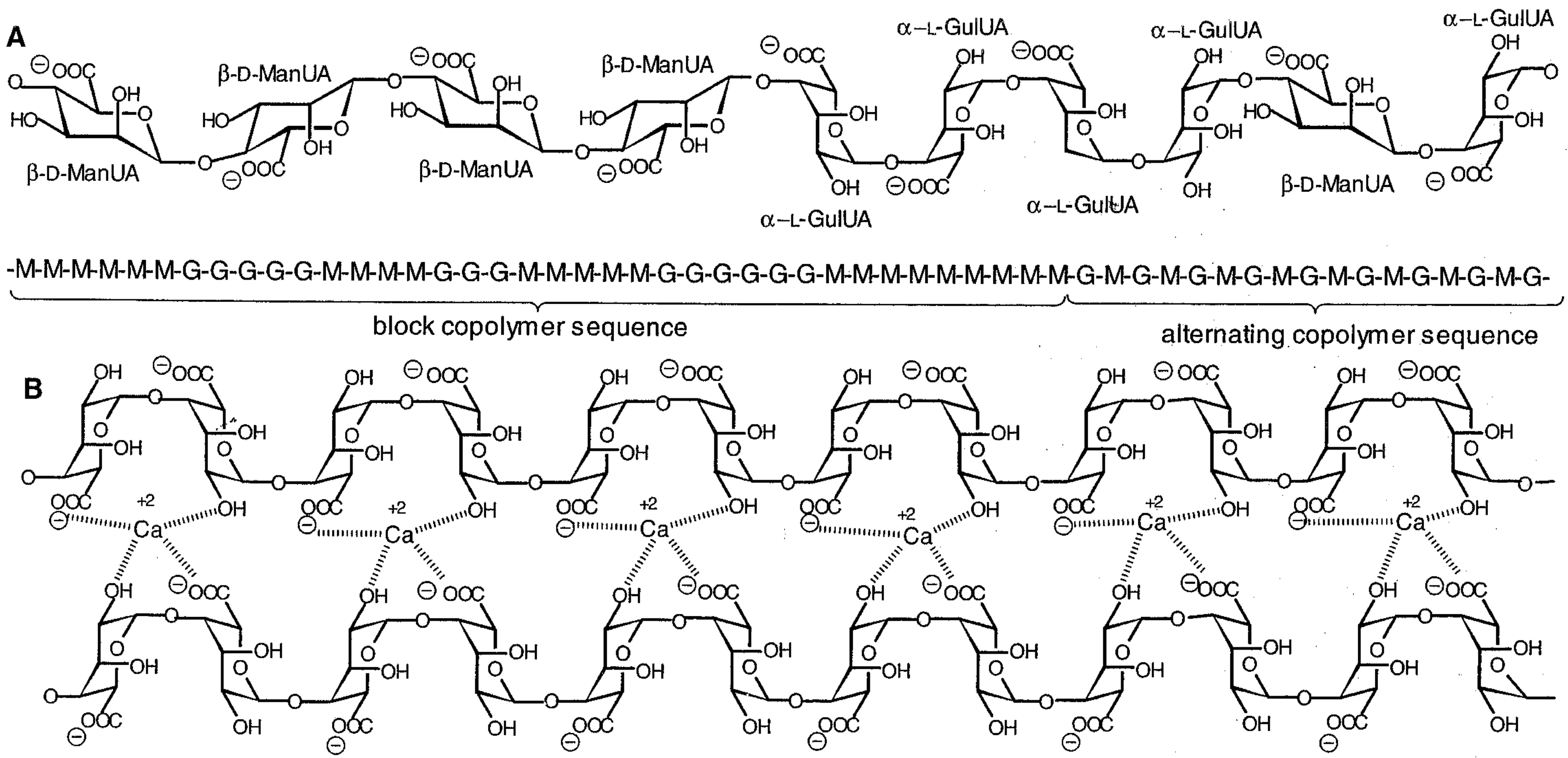
- Alginic acid is insoluble but alkali metal salts are freely soluble in water
- Gels are formed in the presence of Ca^{2+}
- Junction zones are formed by G-stretches in an egg-box structure (one Ca^{2+} complexed by four G)



The junction zone of an alginate gel. The junction zone (shaded) consists of two strands of contiguous guluronate residues, terminated by sequences containing mannuronate residues.

- Ca^{2+}-alginate gels do not melt below the boiling point of water

Cellulose, hemicellulose and fiber



Structures of alginic acid: **A,** structure of a segment of alginic acid; **B,** structure of the calcium alginate gel by the complexing of calcium ions with α-L-guluronate blocks—the so-called egg box structure.

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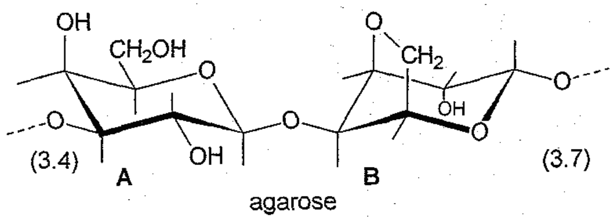
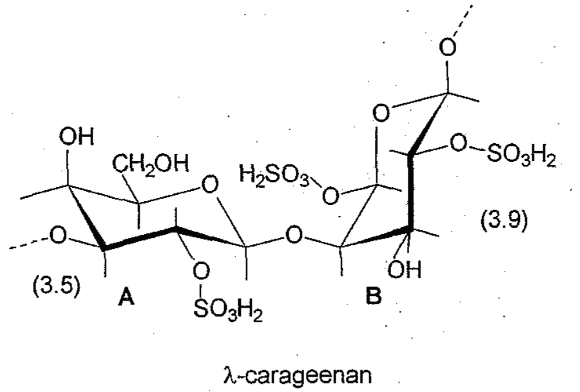
Cellulose, hemicellulose and fiber

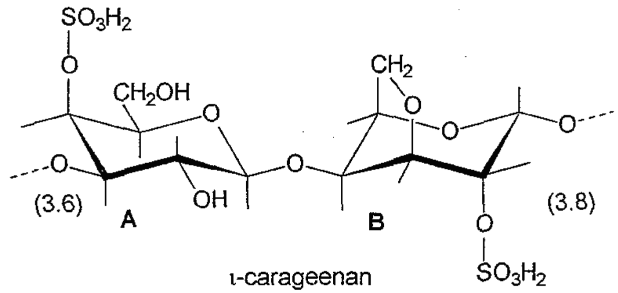
- <u>Agars and carageenans</u>:
  most are linear polymers of galactose derivatives with a general formula …→3)Aβ(1→4)Bα (1→3)Aβ(1→4)Bα(1→3)…..

The monosaccharides of agar and carageenans. The structures of some of the monosaccharide units listed here are shown in Figure → There is a steady increase in the sulfate content as one goes down the list from agarose to μ-carageenan, which is matched by a steady decrease in gelling power; λ- and μ-carageenans will not gel at all.

		Position A	Position B Major	Position B Minor
Agarose		I	IV	
κ-Carageenan		III	V	VI–VIII
ι-Carageenan		III	VI	VIII
λ-Carageenan		I, II	VIII	
μ-Carageenan		III	VII	V, VIII
I	β-D-Galactose			(3.4)
II	β-D-Galactose 2-sulfate			(3.5)
III	β-D-Galactose 4-sulfate			(3.6)
IV	3,6-Anhydro-α-L-galactose			(3.7)
V	3,6-Anhydro-α-D-galactose			
VI	3,6-Anhydro-α-D-galactose 2-sulfate			(3.8)
VII	α-D-Galactose 6-sulfate			
VIII	α-D-Galactose 2,6-disulfate			(3.9)







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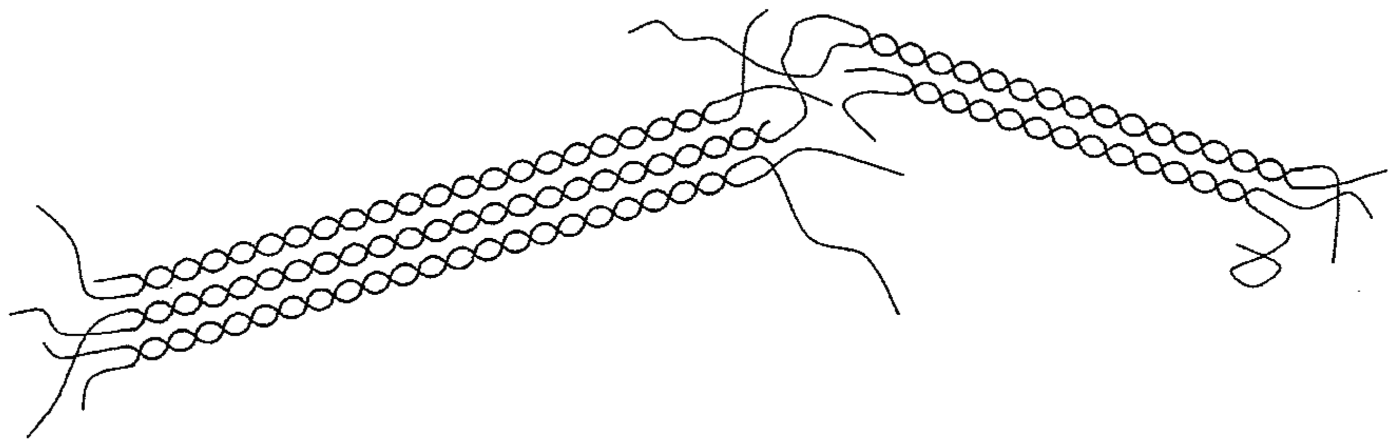
Cellulose, hemicellulose and fiber

- Gelation first involves the formation of double helices of the galactan chains that then form ‘superjunctions’
- Superjunctions only arise when disulfate groups are neutralized by K^+ for κ-carageenan and Ca^{2+} for ι-carageenan



Carageenan or agar ‘superjunctions’.

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Cellulose, hemicellulose and fiber

- Gums
  - Gums are obtained as plant exudates or secreted by bacteria (xanthan gum and gellan)
  - Great affinity for water and form highly viscous solutions
  - Do not form gels (see structure for explanation)
  - Examples: gum tragacanth (from the tree *Astralagus gumnifer*) and guar gum (from the endosperm of the seeds of the leguminous shrub *Cyamopsis tetragonoloba*)
  - Are used as thickening agents to replace starch and to smoothen the texture of ice-cream
  - Guar gum retards the digestion and absorption of carbohydrates because sugars and starch fragments get trapped in the guar gum and are less accessible for digestive enzymes

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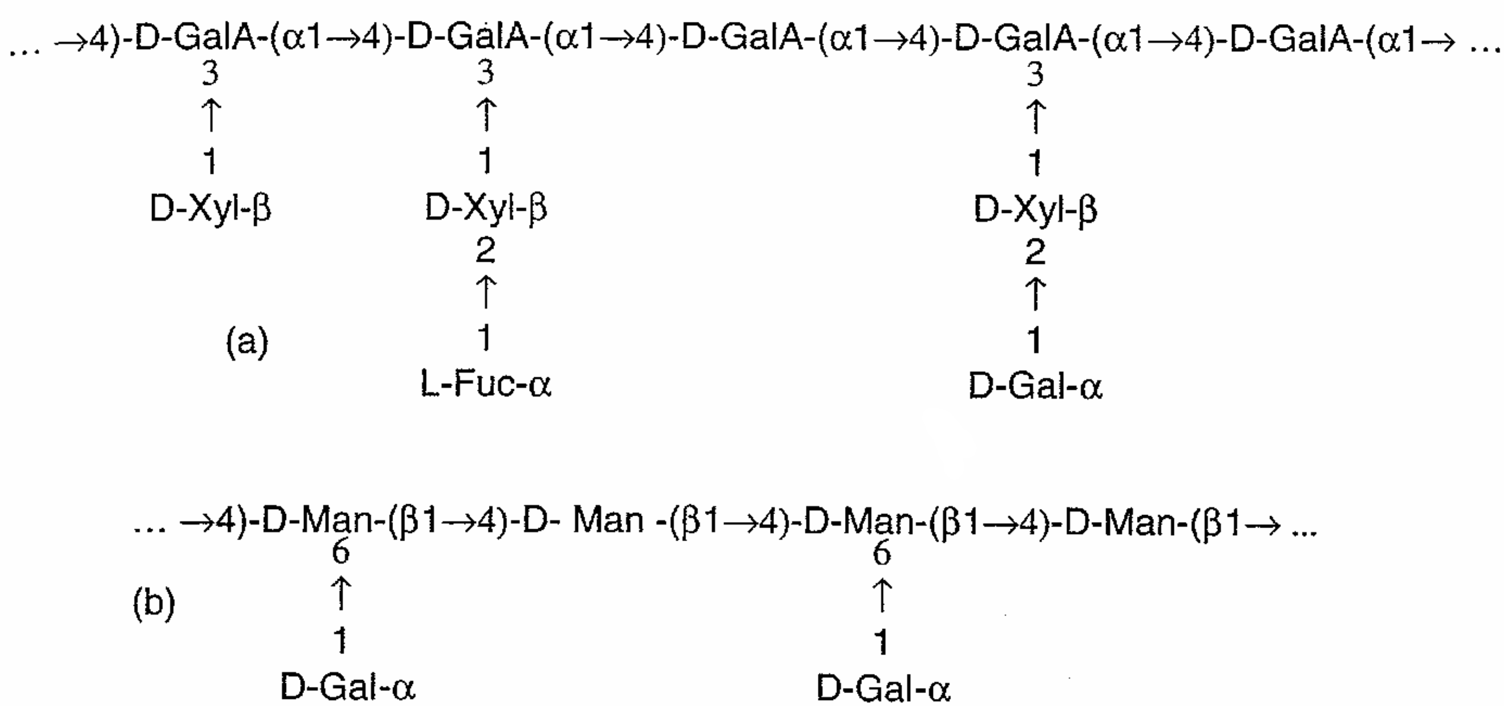
Structure of gum tragacanth and guar gum



(a) *Gum tragacanth. Shown here is the structure of its principal component, tragacanthic acid. The backbone of* D-*galacturonic acid residues has occasional insertions* L-*rhamnose. Almost all the backbone residues carry one or other of the* D-*xylose based side chains shown. (*L-*Fuc, i.e.* L-*fucose, is 6-deoxy-*L-*galactose.)* (b) *Guar gum. Alternate backbone residues carry single* D-*galactose residues. Another galactomannan, locust bean gum (from* Caratonia siligua*), differs from guar gum only having a lower frequency of* D-*galactose side chains.*

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Cellulose, hemicellulose and fiber

- Gums
  - Xanthan gums are produced by the bacterium *Xanthomonas campestris*
  - Gellan gum is produced by the bacterium *Pseudomonas elodea*
  - Xanthan gum molecules contain 10,000–250,000 sugar units
  - Xanthan gums are polymers of glucose $\beta 1 \rightarrow 4$ linked, as in cellulose; every fifth glucose unit carries a trisaccharide that contains 1 or 2 carboxyl groups ⇨ high affinity for water
  - Applications in salad dressings and ketchups

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Structure of xanthan gum and gellan gum

(a)

… →4)-D-Glu-(β1→4)-D-Glu-(β1→4)-D-Glu-(β1→4)-D-Glu-(β1→4)-D-Glu-(β1→4)- …

3	3
↑	↑
1	1
6-Ac-D-Man-α	6-Ac-D-Man-α
2	2
↑	↑
1	1
D-GluA-β	D-GluA-β
2	2
↑	↑
1	1
D-Man-β	D-Man-β

(b)

… →4)-D-Glu-(β1→4)-L-Rha-(β1→3)-D-Glu-(β1→4)-D-GluA-(β1→4)-D-Glu-(β1→ …

↑

…4)- Rha-(β1→3)-D-Glu-(β1→4)-D-GluA-(β1→4)-D-Glu-(β1→…

↑

(a) *Xanthan gum. The trisaccharide side chains are carried on approximately every other glucose unit of the backbone. The mannose residues next to the backbone have acetyl groups (CH_3CO-) attached to the C-6 hydroxyl. Approximately half the terminal mannose residues have a pyruvate residue bridged across their C-4 and C-6 hydroxyl groups.* (b) *Gellan gum. In its native form the glucose residues arrowed here carry an acetyl group on the C-6 hydroxyl and a glyceryl group ($CH_2OH.CHOH.CO$-) on the C-2 hydroxyl. If they are left in place gellan forms very elastic gels. These substituents are normally removed during the manufacture of gellan.*

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